This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Self-assembled and Pyrolyzed Carbon Aerogels: an Overview on Preparation Mechanisms, Properties and Applications

Ahmad Allahbakhsh and Ahmad Reza Bahramian*

An overview of the synthesis conditions and mechanisms for the fabrication of different types of carbon aerogels, as well as structural and functional properties of these materials, is presented here. In this overview, carbon aerogels are classified into three major categories: (i) conventional pyrolyzed organic-based carbon aerogels, which are products of the pyrolysis process of organic aerogels; (ii) self-assembled carbon aerogels, which are products of a reduction process; and (iii) nanocomposite carbon aerogels. Synthesis mechanisms for the sol-gel process of organic aerogels are covered using different suggested mechanisms in the literature. Moreover, the overall fabrication process of self-assembled carbon aerogels (graphene and carbon nanotubes aerogels) is covered and the suggested mechanism for the gelation process of self-assembled carbon aerogels during the reduction process is investigated using reported mechanisms. Structural performance and functional properties (electrochemical and thermal properties) of different types of carbon aerogels are covered in details. Moreover, different structural features of carbon aerogels and the influences of synthesis conditions on these structural characteristics are assessed and compared. Based on literature results covered in this review paper, carbon aerogels are perfect candidates for the fabrication of ultra-low density supercapacitors, as well as thermal insulating materials.

1. Introduction

In classic categorization of aerogel materials, carbon aerogels are defined as a class of porous materials with very low densities, which are the product of the pyrolysis process of an organic aerogel. With enormous developments in the field of graphene- and carbon nanotubes-based aerogels during last decade, however, the word "carbon aerogel" cannot be just dedicated to a specific class of conventional pyrolyzed organic-derived aerogels anymore. Interestingly, new members of this category (e.g. graphene- and carbon nanotubes-based aerogels) presented even more fascinating properties and structural characteristics than the old ones.

The idea of carbon aerogels was first developed by Pekala and coworkers during 1990s, which presented a method for the fabrication of carbon aerogels from pyrolysis process of organic precursors.1 2 Pekala’s porous material attracted a great interest and the number of articles concerning carbon aerogels increased noticeably in the literature. Synthesis conditions, functional properties and structural tailoring of carbon aerogels were the subject of many articles and review papers during past years, and huge developments have been made in this way.3 5 The structure of carbon aerogels, fabricated from pyrolysis process of organic aerogels, is mostly amorphous and hence, most of the functional properties of these materials are depended on the efficiency of sol-gel polymerization as well as the pyrolysis process. However, structurally ordered carbon aerogels became accessible by introduction of carbon nanotubes hydrogels and aerogels.6 Moreover, fabrication of graphene aerogels during last decade8–10, expanded the area of carbon aerogels from almost fully amorphous materials to ordered ones.

The objective of this review paper, therefore, is to give an overview of the published works in the carbon aerogels category as a whole. This review can be considered as a starting point for those interested in different types of carbon aerogels, and can provide initiating information regarding synthesis processes, structural characteristics and properties of these materials. The opening section of this review is dedicated to the synthesis conditions and mechanisms for the fabrication of different types of carbon aerogels. A brief description of the fabrication steps and mechanisms is presented for each type of carbon aerogels in section 2. The nature of differences between different types of carbon aerogels is in structural characteristics. Therefore, structural characteristics of different carbon aerogels are covered and compared in section 3. The last section of this review paper is about the functional properties and potential application fields for carbon aerogels. The authors have restricted details in this part of the review to electrochemical and thermal properties of different carbon aerogel types, as these two can be considered as the most interested potential applications for these materials.
2. Preparation methods and mechanisms

Based on the preparation method, carbon aerogels can be classified into three major categories: (i) conventional organic-based pyrolyzed carbon aerogels, (ii) self-assembled carbon aerogels, and (iii) nanocomposite carbon aerogels. Final performance and structural characteristics of carbon aerogels differ by the preparation mechanism. The total surface area, pore volume, meso- and micro-porosity, and bulk density are the main characteristics which depend strongly on the aerogel preparation method. Preparation methods used throughout the literature for the fabrication of pyrolyzed, self-assembled and nanocomposite-based carbon aerogels as well as suggested mechanisms for each method are covered briefly in this section.

2.1. Conventional pyrolyzed carbon aerogels

The pyrolysis of organic aerogels is the well-known method for the preparation of carbon aerogels. In this method, an organic precursor aerogel is pyrolyzed in a typical thermal treatment program. Different types of organic sources can be used for the synthesis of organic precursors. Resorcinol/formaldehyde, resorcinol/furfural, cresol/formaldehyde, phenolic novolak/furfural, novolak/methyl ethyl ketone, novolak/hexamethylenetetramine, phenolic resoles/methylolated melamine, phenol/formaldehyde, phenol/furfural, polyurethane based organic aerogels, and poly(vinyl chloride) based organic aerogels are some of the most studied organic systems, used as the precursor for the preparation of carbon aerogels. Resorcinol/formaldehyde (RF), however, can be considered as the most interested organic precursor system, which mostly is prepared through polycondensation sol–gel polymerization of resorcinol and formaldehyde, followed by a drying method.

In a typical sol–gel process of a RF system, a given molar ratio of sodium carbonate as a catalyst (C) is mixed with an aqueous solution of resorcinol (R) and formaldehyde (F) as reactants, and deionized water (W) as solvent. Then, the solution is remained at temperatures in the range of 85–95 °C for gelling and curing in a glass container. Upon completion of the cure cycle, the prepared RF gel should be placed in an agitated acetone bath for solvent exchange process. The acetone-filled gel can then be dried using a drying method, resulting in an organic aerogel. A pyrolysis heating program should next be used to convert the organic precursor to the carbon aerogel. The described above method, known as Pekala’s route, is the most common procedure for the preparation of carbon aerogels.

The polymerization mechanism of RF system is reported to include two main steps: (i) formation of resorcinol anions by hydrogen abstraction (enhanced by OH⁻) and formaldehyde addition to obtain hydroxyethyl derivatives; and (ii) condensation of the hydroxymethyl derivatives and cluster growth (catalyzed by H⁺). Afterward, the growing clusters suddenly become unstable and gelation occurs due to spinodal decomposition. The concentration of used catalyst has a clear effect on the stability of clusters and gelation process.

High catalyst concentrations in an RF sol-gel process leads to the formation of highly branched cross-linked clusters, which are less stable towards spinodal decomposition and as a result, smaller and more interconnected polymer particles form. A schematic diagram of described mechanism and structure of expected cross-linked polymer network of RS system is presented in Figure 1.

The sol-gel processes conditions, including resorcinol to the formaldehyde molar ratio (R/F), resorcinol to the catalyst molar ratio (R/C), and resorcinol to water molar ratio (R/W), dictate the final structure of carbon aerogels. Moreover, selected drying procedure for the preparation of RF aerogels also affects the final structural performance of carbon aerogels. Supercritical drying, freeze drying, and evaporative drying are three drying methods for the preparation of organic precursor aerogels. Due to the capillary forces which arise within the pores throughout evaporative drying, this method is not prevalent for the drying of organic aerogels. However, evaporative drying is suitable when a dense carbon aerogel is needed or when the control on the pore size is essential.

Highest pore volume and the widest texture range are accessible via supercritical drying, as the original pure texture of carbon aerogels can be saved through this method. In a typical CO₂ supercritical drying procedure, the water in the pores is first replaced by acetone to reduce the drying time. The acetone is then replaced by liquid CO₂ in a reactor under pressure. Finally, the temperature is raised to the critical point of CO₂ under pressure to remove CO₂. Some structural shrinkages are unavoidable in this drying process due to residual solvents, which remain after exchange steps and can lead to residual surface tensions. These tensions are more when CO₂ supercritical drying procedure is used for the low-density carbon aerogels. Mentioned shrinkage can only be completely avoided with high R/C and R/W ratios.
prolonged solvent exchange steps can reduce shrinkage when R/C ratio is low.\(^5\)

The monolith and low density aerogels are very difficult to obtain by freeze-drying, because of the appearance of huge channels of ice crystal growth during drying process. However, freeze-drying is more economical and easier to operate than supercritical drying method.\(^5,\)\(^38\) During this drying procedure, the wet gel is frozen by immersing its container into the liquid nitrogen to convert water to ice. Afterward, the frozen aqueous solution is removed from the gel by sublimation under low pressures, which this pressure must be lower than the vapor pressure of the frozen solvent at the set temperature. Finally, the residual adsorbed solvent on the solid surface is converted to vapor and removed from the material under very low pressure. The rate of these three steps, which known as freezing, sublimation, and desorption, influences the final pore texture of the aerogel.\(^5,\)\(^41-\)\(^43\)

Catalyst type is another factor, which can affect the final characteristics of carbon aerogels. The size, shape and connectivity of the primary particles strongly depend on the catalyst type and amount used in sol-gel process. Therefore, different types of basic and acid catalysts have been used in the literature to control the structural performance of carbon aerogels. Basic catalysts, however, are more frequent due to their ability to form higher crosslink densities.\(^44\)

Among these catalysts, sodium carbonate is the most interested catalyst for RF system, because of the noticeable structural controllability that is accessible via this type of catalyst. RF organic aerogels synthesized in the presence of sodium carbonate are smaller in particle size when the concentration of catalyst is high, as clusters are less stable with high sodium carbonate concentrations. Formation of hydroxymethyl-derivatives increases at the higher OH\(^+\)/H\(^+\) ratio and consequently, high catalytic concentrations results in highly branched clusters with less stability towards spinodal decomposition.\(^31,\)\(^45\) In addition to widely used sodium carbonate (Na\(_2\)CO\(_3\))\(^46,\)\(^47\), potassium carbonate (K\(_2\)CO\(_3\))\(^46\), potassium hydrogen carbonate (KHCO\(_3\))\(^46\), sodium hydrogen carbonate (NaHCO\(_3\))\(^46\), hexamethylenetetramine (HMTA)\(^12,\)\(^48\), magnesium acetate\(^47\), hydrogen chloride (HCl)\(^49\), acetic acid\(^50\), para-toluensulfonic acid (PTSA)\(^51\), and oxalic acid (OA)\(^52\) are catalysts used throughout the literature for the fabrication of RF organic aerogels. A comparison between structural characteristics of carbon aerogels prepared using different basic and acid catalysts is presented in Table 1.

The final step toward preparation of carbon aerogels from organic precursors is the pyrolysis process. In this step, organic aerogel should be pyrolyzed using a heating program to remove oxygen- and hydrogen-containing groups. Hydrogen elimination during the pyrolysis process leads to the formation of bi-dimensional nanolayers and as a result, a highly interconnected network structure.\(^5\) A typical pyrolysis program for the fabrication of carbon aerogel from organic precursors is presented in Figure 2. The pyrolysis temperature has a direct impact on the final properties of carbon aerogels. Pore volume of carbon gels increases with increasing the temperature in this process. As the carbonization temperature increases, the modification in the porous structure of the gel (more micropores) is expected, as volatile matters release more at higher temperatures.\(^13,\)\(^31,\)\(^52\)

2.2. Self-assembled carbon aerogels

Based on the used source for the self-assembly of carbon aerogels, one can classify self-assembled carbon aerogels into carbon nanotubes aerogels (CNTAs) and graphene aerogels (GAs). However, Wu et al.\(^53\) reported an interesting method for the assembly of carbonaceous hydrogels and aerogels via a one-pot hydrothermal reaction of watermelon. The reported method can be considered as a fascinating procedure for the green fabrication of carbon aerogels. Nevertheless, here we focus on self-assembly techniques for the fabrication of carbon aerogels from carbon nanotubes (CNTs) and graphene oxide (GO) as the starting materials. Final properties and structure of self-assembled carbon aerogels strongly depend on the assembly process and binding conditions. The finishing performance of aerogels also depends on using or eliminating a binder material. Therefore, a clear vision over the self-assembly process conditions seems essential to understand the final performance of this class of carbon aerogels, and to control structural characteristics.

**Table 1.** Structural characteristics of carbon aerogels prepared using different catalyst types

<table>
<thead>
<tr>
<th>Organic system</th>
<th>Organic ratio</th>
<th>Catalyst type</th>
<th>Resorcinol/catalyst ratio</th>
<th>Density ((g/cm^3))</th>
<th>(S_{BET}) ((m^2/g))</th>
<th>(V_{BET}) ((cm^3/g))</th>
<th>(V_{Mic}) ((cm^3/g))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>Na2CO3</td>
<td>50</td>
<td>--</td>
<td>720</td>
<td>0.29</td>
<td>0.39-1.30</td>
<td>46</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>K2CO3</td>
<td>50</td>
<td>--</td>
<td>690</td>
<td>0.27</td>
<td>0.42</td>
<td>46</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>KHC03</td>
<td>50</td>
<td>--</td>
<td>770</td>
<td>0.31</td>
<td>0.70</td>
<td>46</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>NaHCO3</td>
<td>50</td>
<td>--</td>
<td>770</td>
<td>0.30</td>
<td>0.79</td>
<td>46</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.4</td>
<td>magnesium acetate</td>
<td>50</td>
<td>--</td>
<td>723</td>
<td>0.14</td>
<td>--</td>
<td>47</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>PTSA</td>
<td>8000</td>
<td>1.04</td>
<td>751</td>
<td>0.28</td>
<td>0.33</td>
<td>51</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>OA</td>
<td>800</td>
<td>0.86</td>
<td>740</td>
<td>0.32</td>
<td>0.70</td>
<td>51</td>
</tr>
<tr>
<td>Resorcinol/formaldehyde</td>
<td>0.5</td>
<td>HMTA</td>
<td>50</td>
<td>0.18</td>
<td>663</td>
<td>0.24</td>
<td>0.29</td>
<td>12</td>
</tr>
</tbody>
</table>
CNTAs are always fabricated from a stable homogenous suspension of fully dispersed CNTs. Therefore, preparation of such a suspension is the first step toward the assembly process. CNTs cannot be suspended in water or polar solvents in their pure form, despite the presence of some amount of functional groups or dispersant agents on their surface region. Presence of such molecules and their molecular structure affects both dispersion-ability and self-assembly process of nanotubes. Oxidation process is a simple and efficient method for the preparation of stable exfoliated graphite-based nanomaterials suspensions without using any surfactant or stabilizing agents. Oxidized-CNTs readily can be dispersed in water to form suspension, when they acquire negative surface charge. Therefore, sonication of oxidized CNTs suspension results in a stable exfoliated suspension, which can be used for the self-assembly purpose.

In addition to the oxidation process, using different types of dispersant agents is reported to be a promising method for the preparation of a stable CNTs suspension. Dispersant agents should have appropriate active sites to incorporate in the gelation process. Chen et al. used ferrocene-grafted poly(p-phenyleneethynylene) (PPE) as a dispersant agent for the fabrication of CNTs organogels from single-walled carbon nanotubes (SWNTs). They show that presence of aromatic functional groups, which can form π–π interactions between SWNTs surfaces, result in a cross-linked 3D nanotube network in the solution. Chemical structure of PPE as well as proposed mechanism for the formation of 3D network of SWNTs by cross-linking CNTs via π–π interactions between ferrocenyl groups of SWNTs and the neighboring CNTs surfaces, are presented in Figure 3.

Sodium dodecylbenzene sulfonate (SDBS) is also reported as an efficient surfactant for the preparation of graphite-based nanomaterials stable dispersions. Bryning et al. stated that the sufficient surfactant/CNT weight ratio was 5:1 and that higher CNT concentrations result in aggregation. Chitosan is also reported as an efficient sustainable dispersion agent for CNTs, which provides homogeneous suspensions. Conjugated-block-copolymers are another class of dispersants, which contain conjugated-polymer-blocks as well as non-conjugated ones, as shown in Figure 4. The conjugated polymer blocks can establish π–π interactions with CNT wall, while the non-conjugated polymer blocks provide the de-bundled CNTs with a good solubility and stability in a wide range of organic solvents.

Once a stable dispersion of CNTs is prepared, one can fabricate CNTAs via either physical or chemical gelation of CNTs suspension, followed by an appropriate drying process. Physical gelation of oxidized-CNTs can be achieved in CNTs concentrations ≥ 0.3 wt. %. In addition, in the case of oxidized-multi-walled nanotubes (MWNTs), a viscoelastic gel is expected at concentrations around 8 wt. %. Bryning et al. poured SDBS-stabilized-CNTs suspension into a cylindrical mold and prepared a CNTAs through overnight physical gelation followed by a freeze drying step. They also prepared polyvinyl alcohol (PVA) reinforced aerogels through solution diffusion of PVA chains into the CNTs 3D network after fabrication of CNTs hydrogels.
Chemical crosslinking of dispersed CNTs suspension involves using a binder material and/or dispersant agent groups to form a 3D CNTs network. In this method, assembled-aerogel is more consolidated and performs enhanced structural characteristics. PPE is a dispersant agent with the capability to form 3D CNTs network through π-π interactions between PPE aromatic functional groups and SWNT surface (see Figure 4). Kohlmeyer et al.\textsuperscript{59} used this chemical crosslinker besides ferrocene-grafted poly((p-phenyleneethynylene)-alt-(2,5-thienyleneethynylene)) (Fc-PETE) to form a set of CNTAs. They used different CNTs:chemical crosslinker mass ratios to investigate the influences of crosslinkers amounts on the structure of aerogels. They reported that it took about one week to form CNTs hydrogels from CNTs suspensions, and they used CO\textsubscript{2} supercritical drying method to prepare CNTAs from solvent-exchanged hydrogels.\textsuperscript{7,59} They also annealed prepared CNTAs to investigate effects of annealing conditions on electrical and mechanical performance of final aerogels. Stabilized suspension of dispersed CNTs and chitosan can also be converted into a CNTA using ice segregation induced self-assembly method, as reported by Gutierrez and coworkers.\textsuperscript{56} In their study, functionalized MWNTs were stabilized using chitosan and then, the suspension was maintained at a constant temperature around \(-196^\circ\)C and at ambient pressure. Prepared hydrogel was freeze-dried to form a 3D network of MWNTs, crosslinked via chitosan macromolecules.\textsuperscript{58} They also show that MWNTs content as well as freezing direction through hydrogel fabrication, can affect morphology and conductivity of final CNTAs.

In addition to chitosan, other green dispersants and crosslinkers can also be used for the fabrication of CNTAs. Kwon and coworkers\textsuperscript{60} used silk fibroin as a crosslinker to prepare MWNTs aligned and non-aligned cryogels through a procedure shown in Figure 5. In their procedure, MWNTs/silk fibroin suspension was cross-linked at 60 °C during a few days. Ice segregation method is used to form MWNTs aligned cryogels. Structure, morphology and functional properties of fabricated CNTs cryogels strongly depend on the preparation procedure and MWNTs concentrations.\textsuperscript{60} DNA/protein-guided assembly can also be used for the preparation of SWNT/aerogel, as reported by Ostojic et al.\textsuperscript{61} They prepared CNTAs through crosslinking of SWNTs/single-strands DNA/streptavidin suspension. They claimed that four single-stranded DNA in a DNA/streptavidin complex bind two SWNTs and as a result, a 3D SWNTs network cross-linked via DNA strands can be fabricated.\textsuperscript{61} A nondestructive method based on the assembly of CNTs 3D networks through π-π interaction of conjugated block copolymers and MWNTs surfaces is also reported by Zou and coworkers\textsuperscript{62} as a promising method for the fabrication of CNTAs. A schematic of the gelation process of MWNTs aerogels using poly(3-hexylthiophene)-b-poly(3-(trimethoxysilyl) propyl methacrylate) (P3HT-b-PTMSPMA) as the crosslinker is illustrated in Figure 6. The lowest MWNTs critical gelation concentration (0.3 mg/mL) for the fabrication of CNTAs is reported when a conjugated block copolymer was used as the chemical crosslinker of MWNTs. The observed low critical gelation concentration is related to the presence of strong interactions between MWNTs, which originate from the chemical bonding of poly(3-trimethoxysilyl) propyl methacrylate).\textsuperscript{62}
In general, structural and physical properties of CNTAs strongly depend on the preparation mechanism as well as fabrication conditions. CNTs concentration through assembly system affects structural density and performance of final aerogel. Moreover, chemical binders can form more stable and consolidated aerogels. These crosslinking chemicals may have a protein, polymeric or even green origins. A comparison between structural performances of self-assembled CNTAs cross-linked using different chemical binders is presented in Table 2.

An almost same overall procedure is reported for the fabrication of self-assembled GAs. The overall fabrication process includes three individual steps: (i) preparation of a stable dispersion of functionalized graphene, (ii) assembly of graphene hydrogel from graphene suspension and (iii) conversion of prepared hydrogel into GA using a drying technique. In all cases, graphene oxide (GO) has been used as the starting point for the self-assembly process. GO can be readily dispersed in water and organic solvents to prepare a stable suspension of dispersed GO. The GO suspension can form a 3D network through the hydrothermal reduction process.

Conditions of the reduction process as well as GO concentrations (C/O atomic ratio) dictate structure and properties of GAs. Two kinds of structures are expected through hydrogen-bonding of GO nanosheets during a reduction process, as reported by Wu et al. Parallel GO nanosheets form ordered structures and non-parallel nanosheets produce amorphous structures. Both structures form during a self-assembly process and final structure of aerogel depends on the ratio of these alternative structures. A schematic representation of two suggested self-assembly mechanisms as well as transmission electron microscopy (TEM) images of these structures are presented in Figure 7.

Table 2 Structural characteristics of CNTAs prepared using different gelation conditions and crosslinkers

<table>
<thead>
<tr>
<th>CNTs type</th>
<th>CNTs content (wt. %)</th>
<th>Dispersant agent</th>
<th>Crosslinking agent</th>
<th>Gelation mechanism</th>
<th>Density (g/cm³)</th>
<th>S_BET (m²/g)</th>
<th>V_microp (cm³/g)</th>
<th>V_meso (cm³/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNTs</td>
<td>20-50</td>
<td>PPE</td>
<td>PPE</td>
<td>chemical crosslinking and CO2 supercritical drying</td>
<td>0.009-0.01</td>
<td>145-635</td>
<td>--</td>
<td>0.49-0.93</td>
<td>59</td>
</tr>
<tr>
<td>DWNTs</td>
<td>20-50</td>
<td>PPE</td>
<td>PPE</td>
<td>chemical crosslinking and CO2 supercritical drying</td>
<td>0.008-0.01</td>
<td>141-684</td>
<td>--</td>
<td>0.46-1.22</td>
<td>59</td>
</tr>
<tr>
<td>MWNTs</td>
<td>9</td>
<td>carboxylic functional groups</td>
<td>silk fibroin</td>
<td>gelation and flash freezing</td>
<td>--</td>
<td>115</td>
<td>0.0098</td>
<td>0.8609</td>
<td>60</td>
</tr>
<tr>
<td>MWNTs</td>
<td>9</td>
<td>carboxylic functional groups</td>
<td>silk fibroin</td>
<td>ice-templating</td>
<td>--</td>
<td>181</td>
<td>0.0251</td>
<td>0.6196</td>
<td>60</td>
</tr>
<tr>
<td>MWNTs</td>
<td>1</td>
<td>P3HT-b-PTMSPMA</td>
<td>PTMSPMA</td>
<td>gelation and freeze drying</td>
<td>0.004</td>
<td>580</td>
<td>--</td>
<td>--</td>
<td>62</td>
</tr>
</tbody>
</table>
Different reduction agents can be used as an aid to the self-assembly process. However, reduction process can be done without using any reducing agents. Xu and coworkers reported preparation of graphene hydrogels through hydrothermal reduction of 1 and 2 mg/mL GO suspensions at 180 °C for 1-12 hours without using any reducing agents. They show that C/O atomic ratio as well as duration of hydrothermal process affect elasticity and conductivity of final products. In addition, GO suspension can be converted into graphene hydrogel through freezing using methanol and dry-ice.

L-ascorbic acid (LAA) is an environmental friendly widely used reducing agent with a promising reducing efficiency in the reduction of GO into graphene. Unlike other reducing agents, such as sodium borohydride or hydrazine, no gas is formed as a by-product of the reduction reaction using LAA, which reduces the probability of inducing damages to the porous structure of GAs. Sui and coworkers investigated the influences of different ratios of LAA to GO on the structure of final GAs. They suggested that LAA:GO ratio should be 1:1 higher to form a proper graphene hydrogel through reduction process at temperatures around 25-80 °C. Moreover, Fan et al. investigated effects of variation in hydrothermal GO reduction conditions on the structural performance of GAs in the presence of LAA as the reducing agent. Results reveal that surface area and porosity of GAs are strongly depended on the GO concentration as well as reduction conditions.

As discussed, different reducing agents as well as crosslinkers can be used for the assembly of graphene hydrogels. Chen and coworkers prepared GAs using various reducing agents such as NaHSO₃, Na₂S, Vitamin C, and hydroquinone. In addition, they show that shape of the 3D architectures can be controlled by changing the reactor type. Moreover, in another work they show that NaHSO₃ can be used as reducing agent as well. Hypophosphorous acid and iodine (HPA-I) solution is also reported as a reducing agent for the hydrothermal reduction of GO suspension.

Table 3 represents a comparison between structures of GAs reduced using different reducing agents. One can also advance the structure of GAs using different crosslinkers to enhance interconnectivity by increasing the number of chemical and physical crosslinks. Bai and coworkers reported that gelation of GO can be promoted by different non-covalent molecular interactions, including hydrogen bonding, π-stacking, electrostatic interaction, and coordination. Structures of several crosslinkers used to prepare graphene hydrogels are presented in Figure 8. They suggested that increasing the bonding force or decreasing the repulsion force between GO sheets result in GO gelation.
Table 3 Assembly conditions and structural characteristics of GAs

<table>
<thead>
<tr>
<th>GO concentrations (mg/ml)</th>
<th>Reducing agent</th>
<th>Hydrothermal temperature (°C)</th>
<th>Hydrothermal duration (h)</th>
<th>BET Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>Density (g/cm³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>284</td>
<td>3.6</td>
<td>0.51</td>
<td>0.018</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>302</td>
<td>4.1</td>
<td>0.63</td>
<td>0.026</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>365</td>
<td>3.9</td>
<td>0.72</td>
<td>0.056</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>473</td>
<td>4</td>
<td>0.95</td>
<td>0.067</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>5</td>
<td>560</td>
<td>3.9</td>
<td>1.09</td>
<td>0.018</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>10</td>
<td>438</td>
<td>4</td>
<td>0.88</td>
<td>0.020</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>20</td>
<td>381</td>
<td>3.9</td>
<td>0.74</td>
<td>0.022</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>302</td>
<td>4.1</td>
<td>0.63</td>
<td>0.026</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>45</td>
<td>40</td>
<td>577</td>
<td>4</td>
<td>1.17</td>
<td>0.025</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>70</td>
<td>40</td>
<td>302</td>
<td>4.1</td>
<td>0.63</td>
<td>0.026</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>95</td>
<td>40</td>
<td>245</td>
<td>3.8</td>
<td>0.46</td>
<td>0.035</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>LAA</td>
<td>95</td>
<td>1.5</td>
<td>394</td>
<td>3.7</td>
<td>1.46</td>
<td>0.042</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>LAA</td>
<td>95</td>
<td>3</td>
<td>189</td>
<td>3.7</td>
<td>1.05</td>
<td>0.048</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>LAA</td>
<td>95</td>
<td>6</td>
<td>148</td>
<td>3.7</td>
<td>0.60</td>
<td>0.061</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>LAA</td>
<td>95</td>
<td>12</td>
<td>136</td>
<td>3.7</td>
<td>0.48</td>
<td>0.079</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>LAA</td>
<td>95</td>
<td>24</td>
<td>133</td>
<td>3.6</td>
<td>0.42</td>
<td>0.085</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>LAA</td>
<td>95</td>
<td>24</td>
<td>121</td>
<td>3.7</td>
<td>0.36</td>
<td>0.098</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>LAA</td>
<td>95</td>
<td>24</td>
<td>150</td>
<td>3.7</td>
<td>0.72</td>
<td>0.099</td>
<td>67</td>
</tr>
<tr>
<td>10</td>
<td>LAA</td>
<td>95</td>
<td>24</td>
<td>156</td>
<td>3.7</td>
<td>0.93</td>
<td>0.067</td>
<td>67</td>
</tr>
<tr>
<td>0.5</td>
<td>HPA-I</td>
<td>90</td>
<td>12</td>
<td>35</td>
<td>--</td>
<td>--</td>
<td>0.006</td>
<td>73</td>
</tr>
<tr>
<td>1</td>
<td>HPA-I</td>
<td>90</td>
<td>12</td>
<td>59</td>
<td>--</td>
<td>--</td>
<td>0.009</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>HPA-I</td>
<td>90</td>
<td>12</td>
<td>119</td>
<td>--</td>
<td>--</td>
<td>0.011</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>HPA-I</td>
<td>90</td>
<td>12</td>
<td>157</td>
<td>--</td>
<td>--</td>
<td>0.013</td>
<td>73</td>
</tr>
<tr>
<td>1.5</td>
<td>NaH₂SO₄</td>
<td>95</td>
<td>3</td>
<td>95</td>
<td>2-100</td>
<td>0.28</td>
<td>0.042</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>Gallic acid</td>
<td>95</td>
<td>8</td>
<td>299</td>
<td>--</td>
<td>--</td>
<td>0.013</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Gentisic acid</td>
<td>95</td>
<td>8</td>
<td>109</td>
<td>--</td>
<td>--</td>
<td>0.014</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Protocatechu ic acid</td>
<td>95</td>
<td>8</td>
<td>140</td>
<td>--</td>
<td>--</td>
<td>0.016</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Vanillic acid</td>
<td>95</td>
<td>8</td>
<td>184</td>
<td>--</td>
<td>--</td>
<td>0.012</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Ferulic acid</td>
<td>95</td>
<td>8</td>
<td>347</td>
<td>--</td>
<td>--</td>
<td>0.017</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>--</td>
<td>85</td>
<td>72</td>
<td>867</td>
<td>8.6</td>
<td>1.90</td>
<td>--</td>
<td>64</td>
</tr>
</tbody>
</table>

Ji and coworkers used glucose, β-cyclodextrin and chitosan as reducing agents in order to control and tailor the structure and morphology of GAs. Morphology of prepared GAs using each crosslinker is compared with the morphology of GA prepared without any crosslinker in Figure 9. They show that following same self-assembly procedure with glucose, β-cyclodextrin, and chitosan solutions, employing the same recipe of the graphene-based aerogels' gelation, but without GO, do not result in formation of hydrogels. This indicates that these carbohydrates (glucose, β-cyclodextrin, and chitosan) play a reducing agent role in the GO self-assembly process.
2.3. Nanocomposite carbon aerogels

Nanocomposite carbon aerogels can be classified into three categories: polymer/graphene aerogels (PGAs), polymer/CNTs aerogels (PCNTAs) and graphene/CNTs aerogels (GCNTAs). PGAs are mostly prepared through sol-gel polymerization of RF systems in the presence of GO in the sol phase. In this process, a stable suspension of GO with a desired GO concentration can be mixed with specific resorcinol:formaldehyde and resorcinol:catalyst (sodium carbonate) ratios under sonication to form a so-gel mixture. The sol-gel mixture then should be placed in a mold and sealed to cure at a cure temperature around 85-90 °C for 12 to 72 h. The resulting gel can then be solvent exchanged with acetone and dried using supercritical CO₂. Prepared organic-based aerogel can be pyrolyzed then to form a PGA.

Lee et al. reported a very same procedure for the fabrication of polyethyleneimine-modified PGAs. They have modified GO surface with polyethyleneimine (PEI) to prepare a modified-GO suspension, which then was used for the fabrication of PGAs. Preparation procedure used by Lee et al. for the fabrication of PGAs is depicted in Figure 10. PEI, however, can also directly be used as a crosslinker to form PEI-graphene aerogel, which can be pyrolyzed to form PGAs. Other organic systems (such as phenol-formaldehyde and resol) and polymers (such as poly(amic acid), poly(dimethylsiloxane) and polystyrene sulfonate) can also be used as the crosslinker to form PGAs.

The sol-gel polymerization of RF system, described above, can also be used for the fabrication of PCNTAs. Presence of CNTs in the sol mixture during polymerization of RF systems results in a CNTs 3D network cross-linked via polymacromolecules. Prepared organic-based hydrogel can be dried and pyrolyzed to form PCNTAs. Moreover, Kim and coworkers reported a method for the fabrication of poly(dimethylsiloxane) (PDMS)/SWNTs aerogels. In this method, vacuum suction was used to backfill CNTA with PDMS followed by curing PDMS at 70 °C. The resultant PDMS/SWNTs composite aerogel was highly bendable, deformable, and stretchable. With using a mixture of GO and CNTs as the precursor of the self-assembly fabrication process, one can prepare GCNTAs through the hydrothermal process. Hydrothermal reduction of GO and CNTs suspension can be done with and without using a reducing agent. Fan et al. reported preparation of GCNTAs using LAA as the reduction agent for the hydrothermal reduction of GO/MWNTs stable suspension. Zhang and coworkers reported a fabrication method for the preparation of GCNTAs using hydrothermal reduction of GO/CNTs suspension without using any reducing agent. They suggested three possible mechanisms for the hydrothermal reduction of GO/SWNT suspension, shown in Figure 11. Zhang et al. suggested three following mechanisms for the hydrothermal reduction of GO/SWNTs suspension: (i) recovery of π-π conjugations through elimination of OH and H groups at the edge of GO nanosheets during reduction process, (ii) crosslinking of hydroxyl and carboxylic groups, presence at the surface of GO and oxidized-SWNTs, and (iii) formation of 3D network through vacancies and topological defects, forming through release of carbon dioxide during thermal treatment. Zhang and coworkers suggested also that these mechanisms could occur in parallel during the hydrothermal reduction process of GO/SWNTs system.

![Figure 10](image-url) Preparation procedure for the fabrication of PGAs (Reproduced with permission. Copyright 2013, Elsevier B.V.).

![Figure 11](image-url) Suggested mechanisms for the hydrothermal reduction of GO/SWNT system (Reproduced with permission. Copyright 2013, Elsevier B.V.).
3. Structural characteristics of carbon aerogels

Structural performance of a carbon aerogel is strongly dependent on fabrication conditions as well as nature of precursor. The gelation process of carbon aerogels, prepared through well-known sol-gel method, initiates with formation of primary nanoparticles from sol suspension. Primary nanoparticles, then, aggregate to form clusters which in turns, crosslink to form secondary nanoparticles.

Secondary nanoparticles in the structure of conventional pyrolyzed carbon aerogels are expected to have a semi-spherical geometry. Spherical geometries of secondary nanoparticles in the structure of carbon aerogels prepared through pyrolysis of a set of controlled RF systems are depicted in Figure 12.

In conventional aerogels, however, an inter-particle neck presence between two adjacent secondary nanoparticles, which controls structural and physical performance of aerogel. Thermal conductivity, electrical resistivity and mechanical strength of aerogels are directly influenced by this neck region. Interconnectivity of secondary nanoparticles is directly affected by density of aerogel. The higher concentration of polymer chains in the structure of aerogel results in higher connectivity of spheres and smaller porous volumes.

Figure 13 shows the dependency of secondary nanoparticles geometrical state on the density of aerogel for a polyurea aerogel (PUA) fabricated through sol-gel polymerization.

Size of spherical nanoparticles is also a structural characteristic of CAs, which strongly depends on the fabrication process. Presence of surfactants in the sol suspension, through sol-gel
process, is reported to result in formation of more spherical-like nanoparticles. Moreover, Wu and coworkers reported that higher surfactant concentrations led to the smaller particle sizes and the greater dispersed intermediate numbers.

Regarding influences of sol-gel conditions on porosity, detailed studies by Mirzaeian and Hall revealed that R/C ratio dictated total pore volume of RF gels. The noticeable influence of R/C ratio on porosity of RF systems is related to the effects that this ratio has on inter-particle crosslink density. Resorcinol anions form through reaction of resorcinol and formaldehyde in the presence of catalysts, which are more reactive than uncharged resorcinol molecules. Therefore, crosslinking process increases in the case of more R/C ratio and as a result, mesoporosity of the RF gel increase. Mirzaeian and Hall suggest that high catalyst contents in the sol-gel polymerization process results in formation of small secondary nanoparticles, which in turns leads to the formation of microporous structures. On the other hand, low catalyst contents through polymerization process results in formation of larger nanoparticles and development of mesoporosity.

Solvent exchange, drying, and carbonization process does not significantly affect the elastic behavior of RF gels. Porosity is the other important microstructural characteristic of CAs which strongly depends on synthesis conditions, solvent exchange, drying, and carbonization process. Schaef and coworkers suggested that porous structure of RF gel originates from nanoscale phase separation in the sol-gel precursor, which induced and limited by crosslinking process. They suggested that branched polymer system becomes incompatible with the solvent through crosslinking. This incompatibility results in nanoscale phase separation, which in turns leads to the formation of porous structure of RF gels. Regarding influences of sol-gel conditions on porosity, detailed studies by Mirzaeian and Hall revealed that R/C ratio dictated total pore volume of RF gels. The noticeable influence of R/C ratio on porosity of RF systems is related to the effects that this ratio has on inter-particle crosslink density. Resorcinol anions form through reaction of resorcinol and formaldehyde in the presence of catalysts, which are more reactive than uncharged resorcinol molecules. Therefore, crosslinking process increases in the case of more R/C ratio and as a result, mesoporosity of the RF gel increase. Mirzaeian and Hall suggest that high catalyst contents in the sol-gel polymerization process results in formation of small secondary nanoparticles, which in turns leads to the formation of microporous structures. On the other hand, low catalyst contents through polymerization process results in formation of larger nanoparticles and development of mesoporosity.
The microporosity of RF gels does not depend on the nature of solvent used for the solvent exchange process.\textsuperscript{114} Moreover, drying process does not affect microporosity of organic gels.\textsuperscript{110} Mesoporosity, however, is reported to be affected by applied drying method.\textsuperscript{110} Compared to supercritical drying, freeze-drying is reported to result in formation of larger mesopores in RF aerogels.\textsuperscript{115} As discussed before, the main reason for the formation of such a mesoporous structure is ice crystal growth, which takes place during the freeze-drying process.\textsuperscript{116} Moreover, carbonization process is reported to impact microstructure of CAs, as some micropores take place during pyrolysis of RF systems.\textsuperscript{111} Generally, it has been suggested that carbonization of RF systems results in more meso- and microporosity and larger surface area.\textsuperscript{111}

Formation steps, morphology and structural properties of self-assembled GAs, prepared through reduction process in the presence of sodium ascorbate as reducing agent at 90°C, are presented in Figure 16. Based on the used reducing agent, phase separation in the gelation process of GO suspension to GAs can last from one to several hours.\textsuperscript{117-119} However, further hydrothermal reduction results in more reduction of GO nanosheets and more π-π conjugation between graphene structures.\textsuperscript{118} Moreover, long hydrothermal reaction leads to an increase of the intensity ratio of D/G bands in Raman spectroscopy results, which indicates the formation of more reduced graphene nanosheets.\textsuperscript{119} Same structural performance is reported by Ostojic for self-assembled CNTAs.\textsuperscript{61} The presence of D band in Raman spectra of CNTAs, which is associated with K point vibrations, implies a non-covalent gelation process.\textsuperscript{61}

SEM observations reveal that GA structure becomes more tightly assembled with reduction progressing.\textsuperscript{117} Therefore, it can be concluded that gelation process of GAs is based on the reduction of GO nanosheets through the hydrothermal process. In addition, π-π interactions between graphene nanosheets, which are responsible for non-covalent crosslinks in the structure of GAs, increase with hydrothermal reaction time. Rheological behavior of GO suspension through the gelation process shows an almost frequency-independent behavior for storage modulus (G') and an elastic-gel behavior for loss modulus (G'\textsuperscript{\prime}).\textsuperscript{117} Moreover, formation of π-π interactions between reduced graphene nanosheets through the reduction process is obvious in UV-Vis and XPS results. XRD pattern of GAs contain a broad peak at 2θ values around 25°. This peak is reported as the significant peak of π-π conjugated graphene nanosheets in the structure of GAs.\textsuperscript{64, 70, 117, 119}

In the case of PGAs, structural performance of aerogel is also dependent on polymer matrix, besides GO nanosheets. Structural characteristics and morphological properties of PGAs as a function of GO loading contents are presented in Figure 17. XRD pattern of GO loaded phenol/formaldehyde (PF) xerogels, as expected, contains only the broad characteristic peak of GAs and there is no sign of characteristic peak of GO nanosheets, nor peaks of the PF system. Through carbonization process, however, a peak at 44° appeared which is due to the growth of crystalline structures in the PG secondary nanoparticles through pyrolysis. Same behavior is reported for the different loading contents of GO nanosheets in RF systems.\textsuperscript{77, 80}
Worsley and coworkers\textsuperscript{77} reported that morphology of PGAs, prepared through carbonization of GO and RF systems, is strongly dependent on the contents of RF system in PGA. Higher GO to RF contents, results in formation of PGA with no sign of individual RF secondary nanoparticles. A higher content of RF, however, leads to formation of PGA structures with distinguishable secondary nanoparticles. It is helpful to note here that the morphology of activated carbon structures of RF system also changes in the presence of GO nanosheets to sponge-like structure bearing cavities with small pores.\textsuperscript{80} XRD pattern of GCNTAs contain a broad peak around 2\(^\circ\) values, similar to the XRD pattern of GAs.\textsuperscript{93,95,120} This broad peak is related to the non-crystalline \(\pi-\pi\) stacked graphene nanosheets in the structure of GCNTAs.\textsuperscript{94} Such a structural performance is in consistence with morphology of GCNTAs, which is a macro-porous network with graphene nanosheets walls. Shao et al.\textsuperscript{120} suggested that a sandwich morphology form during the hydrothermal process of GO nanosheets with SWNTs stacked between GO nanosheets. Moreover, the ratio of D/G Raman peaks of GCNTAs increases with the content of SWNTs. This behavior is related to the increment of perfect graphitic structures with the increase in the content of SWNTs in the structure of GCNTAs. Structural characteristics and morphology of GCNTAs are shown in Figure 18.

Figure 17. XRD patterns of GO nanosheets, GO loaded PF xerogel (GCPFOX), carbonized PF xerogel (PFx) and carbonized GO loaded PF xerogel (GCPFOX) (a) (Reproduced with permission.\textsuperscript{65} Copyright 2013, Springer Science+Business Media), XRD patterns (b) and SEM images (c) of activated carbonized RF gel (R), 1, 3, 5, and 10 weight % GO loaded carbonized RF aerogels (R\(_{G}\)) and GA (G) (Reproduced with permission.\textsuperscript{75} Copyright 2011, The Royal Society of Chemistry).

4. Properties and applications

During recent years, carbon aerogels have attracted a great interest for many industrial and special applications. High specific surface area, great porosity, enormous electrical conductivity and low density of these materials made them promising candidates for many novel and common applications in different industries. Moreover, high oil uptake of novel GAs and CNTAs, as well as conventional CAs has enlightened an important way for environmental applications of these materials.\textsuperscript{121,123} Plenty of important applications can be named for carbon aerogels such as water purification\textsuperscript{124} catalysts\textsuperscript{4} supercapacitors\textsuperscript{87} and thermal insulating materials.\textsuperscript{125} Electrical performance and thermal characteristics of carbon aerogels, which made them a perfect candidate for the latter two application fields, are discussed throughout this section in details.

4.1. Electrochemical properties and applications

From the very beginning, considerable efforts were devoted on developing novel potential applications for carbon aerogels. One of the most interested applications of carbon aerogels is in the fabrication of highly efficient electrodes, considering noticeable electrochemical and electroanalytical properties of these materials.\textsuperscript{126} Energy is stored in supercapacitors through separation of charge across the electrode/electrolyte interface. Therefore, there are four requirements for a material to be a good electrode: (1) high surface area, (2) high electrical conductivity, (3) high polarizability, and (4) no participation in faradaic reactions.\textsuperscript{127} High current-density, controllable pore size, low electrical resistance, low detection limits and low dependency on convective transport are some advantages of CAs, which consist of the conductor ordered regions separated by disordered insulator parts.\textsuperscript{127,128} High specific surface area (about 750 m\(^2\)/g; see Table 1) of CAs results in lots of available active sites, which facilitate reversible intercalation of lithium ions. Activation of CAs by CO\(_2\) is reported as a promising method for increasing available surface area of CAs. Optimum activation parameters, however, should...
considered to achieve maximum specific surface area from RF system. Moreover, initial pH of RF solution, carbonization temperature and R/C ratio, are three more parameters, which affect specific surface area of CAs. Electrical conductivity of carbon aerogels highly depends on density of pyrolyzed aerogel. Carbon aerogels, prepared through carbonization of RF systems, are reported to have a wide range of electrical conductivity from 5 S/cm for a CA with a density of about 300 kg/m³ to 20 S/cm for aerogel with a density around 600 kg/m³. In addition, a close accordance between elastic performance and electrical conductivity of these materials is reported by Saliger et al. Generally, when features of high electronic conductivity, rapid ion transport and available active sites, all integrate in a material, it can be considered as a perfect candidate for the fabrication of supercapacitor electrodes. Hao et al. hence, tried to present a correlation between capacity and crystalline parameters as well as textual parameters are presented in Figure 19. Results revealed that important electrochemical features of CAs strongly depend on the contents of crystalline and porous structures.

Figure 19. Correlation between the capacity and crystalline parameters (the average crystallite size in the a-axis direction: Lₐ and c-axis: Lₜ) (a), correlation between the capacity and textual parameters (V_{mic}/V_{tot} ratio and S_{EC}) (b), the relationship between S_{AC} and the initial discharging capacity (c), and the relationship between Lₜ and reversible capacity after 50 cycles (graphitized carbon nanofibers: GCNF, RF gel pyrolyzed at 800°C for 2 hours: RFG-1, RF gel pyrolyzed at 850°C for 30 minutes: RFG-2, RF gel pyrolyzed at 800°C for 2 hours after treatment with acid: RFG-3, and RF gel pyrolyzed at 800°C for 2 hours with more porosity: RFG-4) (Reproduced with permission. Copyright 2012, American Chemical Society).

Based on comparisons in Figure 19, presence of both graphitic and amorphous structures, moderate accessible surface areas, and highly interconnected pore channels result in high rate-performance, cycle stability, and lithium-ion storage capacity. In the case of initial efficiency, CA with the highest numbers of crystalline structures (RFG-1) presented the highest efficiency. Moreover, CA with the highest porosity (RFG-2) offered the highest initial charge/discharge capacity, but also the lowest reversible capacities. Furthermore, CA with moderate crystallinity (RFG-4) had the best reversible capacity and rate performance. Hao and coworkers, therefore, suggest that a correlation presence between structural characteristics of CAs and electrochemical performance of these materials. Self-assembled GAs are also reported to have a high-rate supercapacitive performance with specific capacitance values around 211.8 and 278.6 F/g in KOH and H₂SO₄ electrolytes, respectively. The extent of reduction is reported to significantly affect the electrochemical performance of GAs. In addition, Chen and coworkers reported that macropores and surface roughness were two other important factors in the structure of GAs, which affect electrochemical features through enhancement of hydrophilicity/hydrophobicity performance. Electrical conductivity of GAs is reported to vary with the concentration of GO nanosheets in the initial GO suspension. Electrical conductivity of GAs differs from 1.5 × 10⁻² S/m for the GA assembled from 1 mg/ml GO concentration, to 1 S/m for a GA fabricated from 20 mg/ml GO concentration in the initial suspension. In comparison with CAs, PGAs are reported to have larger specific capacitance values (205 F/g), especially at high scan rates. This increase in capacitance of these aerogels is related to the higher specific surface area of PGAs, compared to CA prepared from RF system. Reported specific capacitance for PGAs, however, is still lower than the capacitance of GAs. However, GCNTAs are reported to have a 37% larger specific capacitance (245.5 F/g) in comparison with GAs. This significant increase in capacitance performance of composite aerogels is accompanied by a current density of 2.5 A/g in an aqueous electrolyte. Moreover, a high energy-density of 80.0 Wh/kg is reported for GCNTAs in an ionic liquid electrolyte.

4.2. Thermal insulating properties and applications

Low thermal conductivity of CAs was subjected to a great interest from the very beginning discovery of these materials by Pekala. Porous structure of CAs as well as high IR-extinction coefficient of these materials lead to low thermal conductivity values even at elevated temperatures. More recent studies by Wiener and coworkers revealed that CAs are capable of preserving their porous structure even at ultra-high temperatures. Based on Wiener et al., the total thermal conductivity of CAs prepared from pyrolysis of RF at 1800 °C is expected to be in the range of 0.05-0.5 W/mK. These results are in close accordance with the results reported by Feng et al., which shown that the thermal conductivity of CAs at 1800 °C should be as low as 0.5 W/mK. Therefore, CAs can be considered as perfect candidates for high-temperature thermal insulating applications. As noted before, low thermal conductivity of CAs is related to the porous structure of these materials. Presence of a stable gas (mostly air) in the porosity of CAs results in very low gaseous thermal conductivity values. Moreover, high IR-extinction coefficient of these materials (more than 1000 m²/kg) leads to very low radiative thermal conductivity values.
even at elevated temperatures.\textsuperscript{138} These low contributions of gaseous and radiative thermal conductivities into the total thermal conductivity of CAs made these materials comparable with SiO\textsubscript{2} and polymer aerogels for thermal insulating applications.\textsuperscript{141} Contributions of radiative and gaseous thermal conductivity as well as total thermal conductivity of CAs at elevated temperatures are shown in Figure 20.

Just like other aerogel systems, total thermal conductivity of CAs is closely related to the density of aerogel. As reported by Feng and coworkers\textsuperscript{142}, however, this dependency increase with service temperature. Moreover, it is more likely that the dependency of CAs thermal conductivity is more related to the solid contribution than gaseous and radiative ones.\textsuperscript{149} Reported results\textsuperscript{138-140}, however, prove that the total thermal conductivity of CAs is in a low range even at high temperatures and hence, these materials have a high potential for high-temperatures insulating applications.

\textbf{Figure 20.} Thermal conductivity of CAs as a function of: air pressure at room temperature ($\circ$ : 82 kg/m\textsuperscript{2}; $\times$ : 124 kg/m\textsuperscript{2}; $\Delta$ : 139 kg/m\textsuperscript{2}) (a), aerogel density ($\Delta$ : in air and $\times$ : under pressure) (b) (Reproduced with permission.\textsuperscript{137} Copyright 1993, AIP Publishing LLC), their densities under various temperatures in air (c), measuring temperature in air (d) (Reproduced with permission.\textsuperscript{142} Copyright 2011, Springer Science+Business Media, LLC) as well as gaseous (e), solid and radiative (f), as well as total thermal conductivities (g) of CAs as a function of sample temperature (Reproduced with permission.\textsuperscript{138} Copyright 2009, Springer Science+Business Media, LLC).
supported molybdenum catalyst was catalytically effective in the hydrogenation reaction of acetic acid. Moreover, they suggested that accessibility of the carbon surface to the molybdenum sites as well as the amount and form of doped molybdenum molecules govern all three paths for the reduction of acetic acid (hydrogenolysis, kationization, and consecutive reduction pathways). This is in close accordance with Smirnova et al. report, which argued that pore size of aerogel supports has a huge influence on catalytic performance of metal-doped CA systems. Carbon aerogels prepared from other precursor systems can also be used for the fabrication of catalyst systems. Guilminot and coworkers used a cellulose-based carbon aerogel as platinum catalyst support. An organic aerogel was first prepared from crosslinking of cellulose acetate with polyfunctional isocyanate and by employing supercritical drying method. The prepared aerogel was then pyrolyzed under flowing nitrogen and activated in CO atmosphere. The activation process was followed by an impregnation step to deposit platinum on the structure of activated aerogel. They suggested that pyrolysis temperature could have a great impact on the catalytic performance of metal-doped CAs, as the content of unstable groups in the structure of cellulose-based organic aerogels, which in turns dictates the number of available sites in the structure of final platinum-doped CA, can be controlled by the pyrolysis temperature.

Du et al. prepared a nitrogen-doped CNTA with a high catalytic performance for oxygen reduction reaction (ORR). A MWNTs suspension was first crosslinked through a hydrothermal reaction using pyrrole as the crosslinking agent. The fabricated gel was then pyrolyzed in the presence of pyrrole molecules as “built-in” nitrogen sources. This process resulted in the fabrication of a nitrogen-doped CNTA with a high conductivity (up to 10.9 S/m) and specific surface area (up to 869 m²/g). Prepared nitrogen-doped CNTA presented a remarkable activity toward ORR catalysis in alkaline environment. Moreover, Li and coworkers prepared a recyclable CNTA-supported cadmium sulfide (CdS) as a photocatalyst hybrid system. Fabricated hybrid system had an improved catalytic efficiency, compared to TiO₂ nanoparticles. In addition, it was suggested that CdS nanoparticles grafted on the outside surface of CNTA were active sites in photocatalysis, while other CdS nanoparticles, anchored inside the CNTA, were fresh for use when the catalyst was recycled.

As reported by Yin et al., nitrogen-doped GAs can also be used for the ORR. They fabricated an iron nitride/nitrogen doped-graphene aerogel hybrid catalyst system through a two-step hydrothermal process, including a hydrothermal assembly process followed by an annealing step. Reported results demonstrated that surface area, porosity, density of Fe–N–C active sites, and size of particles on graphene can highly affect the ORR catalytic performance of the system. Wu and coworkers also reported fabrication of a nitrogen-doped GA-supported metal-oxide (Fe₂O₃) catalyst system for the ORR. Their results revealed the importance of 3D macroores and high specific surface area of the GA support, as more positive onset potential, higher cathodic density, lower H₂O₂ yield, and higher electron transfer number for the ORR were achieved when nitrogen-doped GA was used instead of nitrogen-doped carbon black or nitrogen-doped graphene sheets as Feₓ nanoparticles support system. GAs can also be used in the fabrication of high-performance lithium-ion batteries (LIBs). Jiang and coworkers reported the use of a SnS₂/GA system, with high reversible capacity (655 mAh/g after 30 cycles) and excellent rate capability (240 mA/h/g at the rate of 1000 mA/g), as an anode in rechargeable LIBs. Such a performance was related to the high surface area, 3D macroporosity and high electrical conductivity of fabricated 3D structure, as well as improved contact area (and synergistic interactions as a result) between SnS₂ and the graphene. Qiu et al. prepared a TiO₂/GA system with a high-potential applicability as both air purification and LIBs. They used glucose as the crosslinking agent for the hydrothermal assembly of GA in the presence of TiO₂ nanocrystals. Besides enhanced photocatalytic performance, the fabricated system presented excellent specific capacity, high lithium storage, highly reversible capacity, and excellent rate performance. Carbon aerogels can also be used for the fabrication of novel polymeric nanocomposite systems. Huang and coworkers used GAs for the preparation of an inorganic–organic double network hydrogel. They first prepared a graphene hydrogel from hydrothermal reduction of GO nanosheets, and then immersed hydrogel in acrylic acid monomer and polymerize monomers to form a graphene and poly(acrylic acid) nanocomposite aerogel system. The prepared nanocomposite system performed interesting flexibility and electrical conductivity. In addition to discussed potential application fields, carbon aerogels can be considered as candidates for hydrogen storage, fire-resistant systems, heavy metal ions removal systems and oil absorption applications.

5. Conclusions
In this review, synthesis procedure and mechanisms for the fabrication of different types of carbon aerogels, i.e. CAs, GAs, CNTAs, PGAs, PCNTAs and GCNTAs, were discussed and influences of variations in the synthesis conditions on the structure of carbon aerogels were covered. Conventional carbon aerogels are products of the pyrolysis process of organic aerogels and structure of these materials is strongly affected by synthesis conditions. The structure of these materials is also highly depended on the drying process as well as carbonization temperature.

The structures of GAs and CNTAs, on the other hand, is influenced by the concentration of GO and CNTs in the precursor suspensions, respectively. Structural characteristics of these materials are also dictated by the hydrothermal reduction process. PGAs and PCNTAs are products of sol-gel polymerization of an organic system in the presence of graphene (or GO) nanosheets and CNTs in the sol suspension, respectively. The structural performance of these materials is also highly affected by the conditions of the polymerization process, as well as GO and CNTs concentrations. Hydro
GCNTAs are also products of hydrothermal reduction of GO and CNTs. These materials can perform structural characteristics of GAs or CNTAs based on the concentrations of GO and CNTs in the initial sol suspension. Mechanisms for the gelation process of different carbon aerogels were also covered using presented mechanisms in the literature. It is a common believe that formation of primary particle aggregates through sol-gel process results in the formation of secondary nanoparticles, which in turns can form an organic hydrogel through the aggregation process. Regarding the self-assembly process, on the other hand, it is believed that formation of π–π interactions between neighboring nanosheets during hydrothermal reduction process results in formation of elastic hydrogels. Electrochemical and thermal properties of different types of carbon aerogels were also compared in this review. A correlation between structural characteristics and electrochemical properties of CAs was suggested in the literature. This correlation is between electrochemical parameters and crystalline structure of CAs. Consequently, one can tailor electrochemical characteristics of a carbon aerogel supercapacitor via controlling its crystalline structure. Moreover, carbon aerogels perform significant thermal resistance characteristics, even at elevated temperatures, which make them perfect candidates for thermal insulating applications at low temperatures as well as high-temperatures.

6. Outlook and future prospects

A comprehensive overview of recent advances in the carbon aerogels research area was presented in this review paper, with an emphasis on fabrication mechanisms, structural and functional properties, as well as potential application fields. Although the number of publications in the fields covered in this review paper has grown noticeably during recent years, which mostly can be attributed to the recent introduction of new self-assembled members of carbon aerogels’ family (graphene- and CNT-based aerogels), but there are still numbers of unknown aspects regarding fabrication and properties of both conventional organic-based CAs and self-assembled carbon aerogels. For instance, although there are numbers of publications regarding fabrication methods for the assembly of GAs, CNTAs and nanocomposite aerogels, but the nature of gelation process of these materials through the hydrothermal reduction process is not completely discovered, and demands more efforts. The mechanism of the gelation process, including the validity of proposed cluster-aggregation nature of this process, should be confirmed. Moreover, the influences of different reducing and crosslinking agents on the hydrothermal gelation process and structural performance of fabricated gels need more investigations. These are parameters that can affect final performance of carbon aerogels in any application field.

A great progress was achieved regarding fabrication, structure and characteristics of conventional CAs, during past years. As covered in this review paper, structural characteristics and functional properties of conventional CAs have been studied in details in the literature. However, more efforts are needed to fully understand the aggregation process of cluster sub-structures, which in turns control the formation and characteristics of secondary nanoparticles in the structure of conventional CAs. In addition, novel field of carbon aerogel nanocomposite structures, which can gather interesting properties of carbon aerogels and other materials all in a single structure, needs a great attention, as this field can provide a new path for many novel and important applications in this fascinating research area.

Acknowledgements

The authors would like to thank Tarbiat Modares University and Iran Nanotechnology Initiative Council (INIC) for supporting this research work.

Notes and references