Ionothermal Synthesis of Carbon Nanostructures: Playing with Carbon Chemistry in Inorganic Salt Melt

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Solution growth of sp² carbon nanostructures from molecular precursors has been a tremendous challenge as the operation temperature windows offered by most solvents used in wet chemistry synthesis are too low to allow the complete condensation and carbonization of normal simple molecules, such as sugar. Inorganic ionic salt melt has recently enabled direct solution growth of carbon nanostructures with tailored heteroatom doping and porosity, which are indispensable for most functionalities of carbon materials. Compared with molecular solvents (i.e., water and most organic solvents), the ionic salt melt not only provides a wider and higher operation temperature window, but also strong solvation power that ensures the carbonization and precipitation in a controllable manner. Starting from molecules like sugar, this ionothermal process can produce disordered carbon, graphene-like two-dimensional carbon, highly porous carbon nanosheets, etc., depending on the synthetic conditions. Doping of heteroatoms, such as nitrogen, into the resultant carbon can be made by using oxysalt additives such as nitrate, in which N atoms are reduced and finally incorporated into the sp² carbon network. The ionothermal process also can produce nanostructured carbon in a templated fashion in which both salt particles and molecular precursors can serve as the hard or soft template. Due to the favorable microstructure and chemical composition, the ionothermal-derived carbon nanostructures have found diverse applications, as exemplified here by electrocatalysis for oxygen reduction and capacitive energy storage. Further development in ionothermal process will focus on the scalable, green production of carbon nanostructures orientated for commercial applications.

KEYWORDS: Carbon; Ionothermal; Salts melt; Graphene; Energy storage

1. Introduction

sp² hybridized carbons have experienced a renaissance along with the discovery of graphene and the ever increasing demand for efficient energy storage and conversion methods.¹⁻⁵ For most energy-related applications, their performance strongly relies on the magnitude of accessible surfaces and active sites in the nanostructured carbons. Therefore, there has been a continued search of an efficient synthetic method for carbon nanomaterials with tailored structure and chemical compositions. Carbon nanomaterials with high porosity have been accessed in a variety of processes from diverse starting materials. Conventionally, carbons with high porosity have been fabricated by chemical activation based on oxidative removal of weakly bonded carbon atoms;⁶⁻⁷ while in recent years nanostructured carbon with high porosity and tailored microstructure have been obtained in different approaches, such as hard or soft template synthesis, hydrothermal process and topotactical reaction.⁸⁻¹⁷ On the other hand, the doping of carbon by heteroatoms, e.g., N or S atoms, can modify the electronic structure as well as the Fermi level of the host, resulting in the dramatic change in the chemical as well as physical properties.¹⁸⁻²² The synthetic routes to doped carbons generally rely on the use of special starting materials containing these heteroatoms, and therefore cannot be generalized for synthesis of carbons such that doping and structural control can be achieved under simple and similar conditions.

Solution processes, as widely applied for inorganic nanoparticle synthesis, are versatile approaches that enable simultaneous control of the microstructure and size.²³⁻²⁴ However, solution processes are practically not amenable to the growth of carbon nanostructures as the low operation temperature of most solvent, i.e., water or organic solution, cannot allow poly-condensation and carbonization for most molecules. In hydrothermal/solvothermal synthesis, the operation temperature can be higher than the boiling point of the solvent, and indeed carbonization of organic or biomass occurs, while the autogenesis high pressure raises concerns over safety and makes it inappropriate for scalable production. Inorganic salt melt of ionic nature with high chemical stability is the best alternative to these molecular solvent and they provide a wide
working temperature ranging from near 100 to over 1000 °C depending on salt composition. The high working temperature allows the complete carbonization and condensation of most molecular precursors to form pure sp² networks, which otherwise are not possible for most organic (or water) solution under ambient pressure. The ionothermal process therefore appeared as a general solution to nanostreamed carbon synthesis from different molecular precursors.35 Besides, salt melt can serve as the solvent for organic reactions as well as the synthesis of different inorganic nanostructures,25–29 and covalent organic frameworks (COFs).30, 31 Particularly, the crystalline form of graphitic carbon nitride can be only accessed by the salt melt synthesis possibly due to the strong ionic, polar environment.32, 33 It has to be noted here that “ionothermal synthesis” has been also connected with material synthesis using organic ionic liquid as the reaction media,33, 34 which however usually ends below 300 °C. In the present review, we discuss carbon synthesis using inorganic, chemically inert salt such as alkali metal chloride, which can solvate certain molecular precursors like carbohydrate,36 and provide a strong ionic and polar liquid environment for carbonization reaction starting from homogeneous solution phase. Oxysalts (such as nitrate) and transition metal salts (such as ZnCl₂) can interact strongly with the carbonization reaction and therefore they can be used as additives to control the growth and doping of the carbon nanostructures. Combined with the recyclability of the salt, the ionothermal process has been regarded as a green and scalable process for the processing of carbon materials.

Herein, we review the recent advances in the solution growth of different carbon nanostructures (Figure 1) from molecular precursors by the ionothermal process. We first introduce the carbon nanostructures synthesis from inert salt of alkali metal chloride and method to access graphene-like carbon structures. Afterwards, we discuss the control of heteroatom doping, high porosity and microstructure in ionothermal growth of carbons. Most carbon nanostructures discussed in this review are synthesized from sugar, while the use of other precursors is also introduced. The applications of the ionothermal derived carbon are then discussed with focus on the electrocatalysis and capacitive energy storage. This review is then finalized by a summary of the current status together with future perspectives of the ionothermal carbon synthesis.

### 2. sp² carbon synthesized by carbonization of sugar in inert chloride salt

#### 2.1 “Cooking” sugar in alkali metal chloride salt

The type of salt used for the ionothermal process has to be selected with care before experiment. General guidelines to follow include: 1) low vapor pressure (to avoid vaporization loss); 2) large operation temperature and 3) chemically inert in the carbonization reaction. The use of alkali metal chloride salt therefore appears to be the natural choice and two component systems with a eutectic temperature are favored due to the low melting point as compared with single component system. One of the frequently used salt systems in ionothermal carbon synthesis is the eutectic LiCl/KCl system, which has a melting temperature of 353 °C.37 Transition metal salts like ZnCl₂ can also be used as it is extremely effective for pore generation in the products, in spite of its high vapor pressure. Typical salt systems used for ionothermal synthesis of carbon are given in Table 1. Oxysalts like nitrate can react with carbon, and they are also not stable solvents for carbonization. However, both of transition metal halides and oxysalts can be used as essential additives which can control the doping and modulate the porosity of the obtained carbon products.

In the LiCl/KCl melt, sugar (such as glucose) undergoes steady polycondensation and carbonization by releasing water molecules upon heating. Mechanistically, it involves several intermediate reactions, and the transformation through cycloadditions into carbonaceous matter of predominantly sp² C–C bonds,38–40 finally resulting in a dense graphitic matter after structural rearrangement upon continued heating. Synthesis of carbon nanostructures by carbonization of carbohydrate molecules in the eutectic LiCl/KCl salt melt have been examined by Liu et al.41 It was found that, for glucose to salt ratio of 1 : 10 (by weight), carbonaceous products can be obtained and the carbon content increases with the reaction temperature. The products obtained at temperatures of 400 °C can contain oxygen of up to 30% and show good dispersity in water, implying the presence of large amount of functional groups (e.g., –OH).
comparison, the products synthesized at higher temperatures (> 600 °C) show irregular structure in the micrometer scale and are not dispersible in water. Figure 2 presents the typical scanning electron microscope (SEM) and transmission electron microscope (TEM) images for the ionothermal carbons. The samples are largely disordered and completely amorphous without graphitic order. The microstructures of the ionothermal carbon differ greatly from that of the product obtained by direct carbonization of the same precursor in nitrogen atmosphere. For instance, the specific surface area (SSA) increases from around 20 m² g⁻¹ for the direct carbonization product, to over 600 m² g⁻¹ for the ionothermal carbons. The maxima porosity is achieved when the pore generation by eliminating volatile species and pore collapsing and closing with increasing temperature reaches equilibrium.

2.2 From irregular structures to graphene-like carbon sheets

With a careful observation of the TEM images (Figure 2c), thin film-like structures can be found clearly, yet in a very small amount. These thin-film structures are greatly enhanced in amount by reducing the concentration of the precursor in the salt melt to 1 : 100 (Figure 3a). From the TEM images shown in Figure 3b–c, these thin-film structures are still disordered, while the electron diffraction (ED) pattern clearly shows the two

Figure 2. Electron microscopy characterizations of ionothermal carbon synthesized at 800 °C (glucose : salt = 1 : 10 by weight). (a) Typical SEM image of the carbon structure. (b) Selected SEM image showing the presence of graphene-like layers. (c) Typical TEM image. The arrows point the graphene-like structures. (d) Typical high resolution-TEM (HR-TEM) image showing amorphous structure without graphitic order. Reproduced with permission from Ref. 41, copyright@2014, John Wiley & Sons, Inc.

Figure 3. Graphene-like structure synthesized by the ionothermal process at low glucose concentration (glucose : salt = 1 : 100). (a–d) Morphological characterization for layered structure by (a) SEM (b) TEM (c) HR-TEM, and (d) atomic force microscope (AFM). The inset in (b) is the corresponding electron diffraction pattern. (e) Comparison of Raman spectra for graphene-like carbons (MS-G800) and ionothermal carbon (MS-C800) with irregular structure (synthesized at high glucose concentration 1 : 10). (f) Photograph of water contact angle (132.1°) for layer structure coated on a glass substrate. Reproduced with permission from Ref. 41, copyright@2014, John Wiley & Sons, Inc.
diffraction rings with low intensities that can be assigned to the graphene (100) and (110) reflections (Figure 3b), which differs from that of the amorphous carbon. The crystallinity can be enhanced by increasing the reaction temperature, while single-crystalline like graphene structures with large domain size cannot be obtained at carbonization temperature up to 1200 °C. The thickness of the graphene-like sheet varies between 0.6 ~ 10 nm. Due to the presence of surface functional groups like C−OH, single layer thickness close to ideal value is not achieved as oxygen atoms bond stably to the sp² carbon network. Use of oxygen-free precursors might result in carbon materials free of oxygen with a cleaner surface. These graphene-like carbon sheets obtained at temperatures higher than 700 °C showed dominating hydrophobicity (Figure 3f), implying that the surface might be terminated by hydrogen rather than −OH. Due to the high surface area and the favorable surface properties, these carbon nanosheets demonstrate high absorption capacity for different organic solutions.41

The mechanism for the formation of graphene-like carbons has been discussed with respect to the structural evolution in salt melt at high (1:10) and low (1:100) precursor concentration. Despite that a series of intermediate step or reactions are involved in the carbonization in ionothermal process, at high precursor concentration inter-connected thick carbonaceous structures already form before salt melting, as confirmed by the SEM observation. These structures remain stable in the further carbonization process after salt melting and only weak bonded functionalities are liberated at high temperatures without destructing the carbon structure. In comparison, in the case of very low precursor concentration, a very different picture appears. The pre-carbonization (and caramelization) product formed before salt melting are thin layered structures (as discussed in Ref. 41), which afterward are solvated and exfoliated in the salt melt and liberate to graphene-like films as a result of solvent effect. Inorganic salt melt have shown to be efficient solvent for the exfoliation of layered graphite and its isoelectronic analog hexagonal BN.42,43

3. Heteroatom doping and growth control of highly porous carbons

3.1 Oxysalt additives as heteroatom sources for doping

Incorporation of heteroatoms, such as nitrogen and sulfur, into...
the sp² carbon network can result in significant change in electronic as well as chemical properties, which are appealing for diverse applications. Use of precursors containing these heteroatoms can enable easy access to these doped carbons, while it is also possible to supply these heteroatoms from the salt melt itself. As shown by Liu et al. nitrate salt, when added as the additive to the LiCl/KCl salt, can exert a significant influence on the carbonization process, leading to a sharp decrease in carbon yield. Interestingly, elemental analysis together with X-ray photoelectron spectroscopy (XPS) reveals that nitrogen atoms are incorporated into the sp² carbon network in the form of pyridinic, pyrrolic, and graphitic C–N bonds. It is surprising that the product is free of NO functionalities, suggesting oxygen is transferred from N to C, presumably in an electro-cyclic reaction (Figure 4). In a similar process, the addition of sulfate salt (by K₂SO₃) to the LiCl/KCl salt melt results in the sulfur doped products. Alternatively, thiosulfate (Na₂S₂O₃) also can supply S atoms to the final carbon product in the chloride salt melt. The chemical bonding of S in the product is however, very different from the case of nitrogen. From XPS, sulfur atoms are present in the product in two distinct forms: thiophenic C–S bonds and sulfonic S–O bonds. This is different from the sulfonated carbon derived from sugar which contains exclusively S. The proposed structures of the planar atomic arrangement of the N and S-doped carbons are given in Figure 4. Sulfur atoms are only found around the edges of the sheet, while nitrogen atoms can be incorporated as graphitic within the hexagonal network. Likewise, phosphorous atoms can be also doped into the sp² carbon by using phosphate salt as additive during molten salt synthesis, in which the bonding to P is presumably in the form of PO₄. From a systematical investigation, it was found that other p-block element cannot be doped by using its corresponding oxysalt as heteroatom source. In spite of the clear chemical characteristic of the obtained doped carbons, the exact reactions involved in the transferring of these heteroatoms from the oxysalt salt in their highest oxidation state to sp² carbons remain to be unraveled, and these reactions may have important implications for organic synthesis.

The oxysalts, such as nitrate and sulfate, dissolved in the LiCl/KCl melt interact strongly with the carbonization process, leading to drastic loss of carbon yield and increase in the surface area of the product (Figures 4c–d). This is mechanistically a reaction similar to the activation process in which weakly bonded carbon atoms (presumably in the form of sp² hybridized C–O, C–H bonds) are oxidized to gaseous CO or CO₂ by the oxysalt anions according to thermodynamics. The maxima SSA can easily reach over 1500 m² g⁻¹ for N-doped carbons and over 2000 m² g⁻¹ for S-doped samples. Surprisingly, a maxima SSA of 3210 m² g⁻¹ is obtained for a S-doped sample (Figure 4d), far exceeding the theoretical value for single layer graphene (~2630 m² g⁻¹). By and large, a higher reaction temperature is favorable for increase the SSA, while at the cost of further loss of carbon yield (Figures 4c–d). This is because more weakly bonded carbons are gasified at higher temperatures, thus opening more pores in the sp² network. However, carbonization at temperatures higher than 1100 °C leads to pore closure and densification by further graphitization. The increase in SSA is in line with the evolution of pore size distribution. The fraction of the micropores is steadily reduced in fraction, while mesopores and macropores grow in fraction with the growing in graphitization temperature.

In the presence of oxysalt, it is interesting that carbon undergoes two-dimensional (2D) growth, yielding smooth planar structure of thickness up to 10–20 nm with large lateral extension. This is apparently not densely packed few-layer graphene sheet as they are in fact highly porous without strict graphitic order. In the N-doped carbons, nanosheets still coexist with small amount of particles, which can be reduced in amount by decreasing the concentration of precursor (glucose). A more careful observation by HR-TEM reveals that the sheets are made up of densely packed ‘tagliatelle’-like nanoribbons, in which the micropores come from the interstitial spaces of the ribbons (Figure 5). The distances between the ribbons are in the range of 0.36 ~ 0.42 nm (Figure 5c), which is typical for aromatic packing, but obviously more expanded than few-layer graphene. In comparison, the S-doped samples demonstrate a very similar microstructure but with higher porosity and thickness. In these samples, the higher electron density as well as the high robustness of 2D layers allows the determination of the localization and co-localization of single heavier atoms such as sulfur. As can be seen from the HR-TEM image (Figure 6), isolated single and chains of black spots, presumably sulfur in a condensed-thiophenic structure, are clearly observed which terminate the edges of the ribbons (Figure 6d). In addition, the scanning tunneling electron microscope (STEM) image demonstrates that the highly porous carbon sheets (Figure 6c), which are macroscopically homogeneous, contains large amount of well-accessible, in-plane micropores.

It has to be noted that both the S and N-doped nanosheets shown in Figure 5 and 6 are synthesized at the precursor.
concentration of 1 : 10 (glucose : salt = 1 : 10). Therefore, 2D growth in this case might be driven by a different mechanism as compared to the graphene-like carbon sheets shown in Figure 3. The formation of layered structure is often found in colloidal system driven by the minimization on interfacial energy. In the present case, a similar mechanism might have been involved. From the above observation, these planar carbon structures demonstrate the highest SSA, good stability and easy accessibility to all edge atoms. To understand the mechanisms of their formation, we captured a series of intermediate product by freezing the reaction at temperatures between 360 ~ 500 °C. Luminescent carbon dots with high content of oxygen and sizes comparable to the thickness of the 2D sheets are obtained. These primary structures presumably undergo self-organization into 2D aggregates via a ‘vectorial alignment’, as found in a similar process. In the later stage with continued temperature rising, the strong oxidizing salts continuously ‘polish’ these structures towards stable and smooth sheets, by removing weakly bonded carbons in form of CO₂. The carbon sheets can be depicted as a ‘noodle-block’ (‘Ramen’) structure with constant nanometer thickness, but composed of self-organized interlinked ribbons, as shown in Figure 7.

### 3.2 2D carbon growth assisted by oxysalt additive

Since nitrate and sulfate can serve as the agent that controls 2D growth, doping and high porosity, it is quite nature to examine the effect of other oxysalts as additives in the controlling of carbonization in salt melt. Oxysalt at the same time behaves as the activation agent that generate pores by oxidative removal of weakly bonded carbon atoms. The general reaction between carbon and oxysalt anions can be written as: C + NmO\textsuperscript{2−} \rightarrow CO (or CO\textsubscript{2}) + Nm (or NmO\textsubscript{2−}), where Nm stand for non-metal p-block element or hydrogen. On the basis of Lux-Flood acid-base theory, hydroxide anions behaviors similarly as other types of oxy-anions in the molten state by establishing an equilibrium according to NmO\textsuperscript{2−} \rightarrow NmO\textsubscript{2−} + O\textsuperscript{2−}. The reduction of Nm oxide by carbon intermediate therefore pushes the reaction towards the right side continuously during carbonization at high temperatures. In fact, alkali metal hydroxides have been long used as activation agent for porous carbon production; while other types of oxysalt (such as chlorate) have similar activation effect as the above redox reaction is energetically favored.

The product obtained from salt melt dissolved with different type of oxysalt other than nitrate and sulfate have been examined in our group. Using the same precursor (glucose, 1 : 10 in mass ratio), it was found that, in addition to nitrate and sulfate, hydroxide, phosphate, carbonate and chlorate have obvious ‘activation effect’, resulting porous carbon with SSA over 1000 m\textsuperscript{2} g\textsuperscript{−1} (as listed in Table 2). However, the microstructure of these carbon varies depending on the additive; only chlorate and carbonate salt can direct a 2D growth and other oxysalts lead on irregular structures. It has to be noted here that borate (added to LiCl/KCl in the form of NaBO\textsubscript{2}) does not behave as a porogen by activation as it cannot oxidize carbon (at temperatures lower than 1200 °C) according to thermodynamics. The detailed discussion regarding energetics of activation and pore generation are given in Ref. 46. Different from the layered carbon derived from LiNO\textsubscript{3}@LiCl/KCl (or K\textsubscript{2}SO\textsubscript{4}@LiCl/KCl) salt melt discussed above, the products obtained from K\textsubscript{2}CO\textsubscript{3}@LiCl/KCl is dominated by much thicker layers of carbon with lateral size in the micrometer range and SSA of over 1000 m\textsuperscript{2} g\textsuperscript{−1}. TEM observation reveals that these sheets in fact comprise large
domain of thin-layer structures similar to that of agglomerated puckered graphenes (Figures 8a−c). In comparison, the products synthesized in the presence of KOH, KH$_2$PO$_4$ and NaBO$_2$ do not show a layered morphology, indicating a different growth mechanism.

The most oxidizing salt additive, KClO$_3$, leads to very uniform 2D growth and high porosity under a wide range of carbonization conditions. Results have shown that the layered carbon structures with SSA close to 2000 m$^2$ g$^{-1}$ can be synthesized at the sugar to salt ration of 1 : 5, doubling the efficiency of production compared with the case of nitrate additive. From the SEM images (Figure 8), the carbon sheets all have very large lateral size (over 10 $\mu$m) with natural wrinkles similar to that of graphene (Figures 8d–f). As the products are obtained in a strong oxidizing salt melt, larger amount of surface functionalities related with oxygen together with high concentration of in-plane pores are present, as evidenced by AFM image (Figure 8f). Due to presence of surface groups, the minimal thickness presumably for a single-layer is around 0.5 nm, while the maximal thickness observed by AFM can be over 5 nm.

From this systematical investigation, a general yet admittedly
incomplete picture for the growth of 2D carbon in salt melt appears. 2D growth of carbon layers from sugar precursors in an inert salt melt relies on the presence of strong oxidizing anions, which not only serves as the porogen, but also actively participates in the growth and organization to form the 2D structures. As can be expected, this mechanism certainly does not limit to sugar precursors; other type of molecules can be also converted to layered carbons in a similar salt system.\(^{51}\) In a more generalized case, the carbonization of organic salt with alkali metal experiences a similar reaction (possibly it first transforms to a mixture of carbonate, hydroxide and carbon intermediate) as in the oxidizing salt melt, resulting in the formation of similar porous layered carbons.\(^{54-58}\)

3.3 Activation for pore generation by zinc chloride

In contrast to inert chloride salts such as LiCl and KCl, transition metal chlorides like ZnCl\(_2\) are reactive and have a much higher vapor pressure. ZnCl\(_2\) in fact has long been used as an activation agent for the production of highly porous carbons from biomass or coals usually by heating at temperatures higher than 800°C.\(^{59-62}\) However, the role of ZnCl\(_2\) solely as the activation agent has been long questioned as compared to other oxidative activation agent such as KOH.\(^{63, 64}\) On the one hand, it has been widely accepted that ZnCl\(_2\) serves as the dehydration agent for cellulosic materials, that is, it eliminates water molecules from the backbone of the precursor and therefore promotes the formation of reactive double bonds of the carbon skeleton and pore generation by cyclo-addition reaction.\(^{65, 66}\) On the other hand, metal chlorides with strong covalency, such as AlCl\(_3\) and ZnCl\(_2\), are strongly acidic and are generally regarded as ‘Friedel-Crafts’-type catalysts that promote the condensation (alkylation and acylation reactions) of aromatic hydrocarbons.\(^{25}\) Besides, practically ZnCl\(_2\) salt is usually heated to temperatures over 1000°C, which far exceeds its evaporation temperature (usually around 450 ~ 500°C).\(^{67}\) Therefore, it is highly possible that ZnCl\(_2\) has been converted to Zn(OH)\(_2\) or ZnO at low temperatures by taking the water from the precursor, and therefore the reduction of ZnO by carbon should be considered in some cases. At least, it is thermodynamically feasible that carbon reduces zinc compounds, thus giving rise to a side path of
Table 3. Characteristics of other carbons derived from different precursors from biomass to ionic liquids, by the ionothermal route using metal chloride and other salt melts.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Salt</th>
<th>Temperature/Duration/synthetic details</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass (Tofu: beancurd)</td>
<td>LiNO$_3$@LiCl/KCl</td>
<td>2 h @ 850 °C</td>
<td>1202</td>
<td>0.84</td>
<td>72</td>
</tr>
<tr>
<td>Biomass (e.g., peanut shell)</td>
<td>59Na$_2$CO$_3$/41K$_2$CO$_3$; CaCl$_2$/NaCl (1:1); 43.5Li$_2$CO$_3$/31.5Na$_2$CO$_3$/25K$_2$CO$_3$</td>
<td>1 h @ 850 °C</td>
<td>316 – 408</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>Biomass (e.g., pine wood chips)</td>
<td>ZnCl$_2$</td>
<td>1.5 h @ 500 °C</td>
<td>1160 – 1624</td>
<td>0.81 – 1.16</td>
<td>74</td>
</tr>
<tr>
<td>Biomass (Glucose, microcrystalline cellulose, and lignin)</td>
<td>KCl/ZnCl$_2$-Eu</td>
<td>2 h @ 1000 °C</td>
<td>974 – 2025</td>
<td>0.788 – 1.507</td>
<td>75</td>
</tr>
<tr>
<td>Biomass (lignin derived from beech wood chips)</td>
<td>KCl/ZnCl$_2$-Eu</td>
<td>2 h @ 240 °C, 2 h @ 850 °C</td>
<td>1240 – 1610</td>
<td>1.0</td>
<td>76</td>
</tr>
<tr>
<td>Biomass (peanut shell)</td>
<td>ZnCl$_2$</td>
<td>1.5 h @ 480 °C</td>
<td>1643</td>
<td>0.42</td>
<td>77</td>
</tr>
<tr>
<td>Adenine</td>
<td>NaCl/ZnCl$_2$</td>
<td>1 h @ 900 °C</td>
<td>1770 – 2900</td>
<td>Max. 5.2</td>
<td>78</td>
</tr>
<tr>
<td>Glucose</td>
<td>KCl/x%ZnCl$_2$</td>
<td>2 h @ 300 °C + 1 h @ 900 °C</td>
<td>280 – 2160</td>
<td>0.22 – 1.74</td>
<td>79</td>
</tr>
<tr>
<td>Glucose@ silica template</td>
<td>ZnCl$_2$</td>
<td>2h @ 1000 °C; Combined salt templating-hard templating</td>
<td>&gt; 2500</td>
<td>3.24 – 4.26</td>
<td>80</td>
</tr>
<tr>
<td>D-glucose and melamine</td>
<td>LiCl/KCl-Eu</td>
<td>5 h @ 550, 850 and 1000 °C</td>
<td>387 – 1190</td>
<td>0.282 – 0.639</td>
<td>81</td>
</tr>
<tr>
<td>Glucose or glucosamine hydrochloride</td>
<td>ZnCl$_2$</td>
<td>&gt; 750 °C</td>
<td>881 – 1208</td>
<td>0.61 – 1.2</td>
<td>82</td>
</tr>
<tr>
<td>Chitosan</td>
<td>ZnCl$_2$</td>
<td>2 h @ 400 – 700 °C</td>
<td>670 – 1582</td>
<td>0.42 – 1.23</td>
<td>83</td>
</tr>
<tr>
<td>Different organic solutions</td>
<td>ZnCl$_2$</td>
<td>550 °C</td>
<td>Max. 1666</td>
<td>Max. 2.80</td>
<td>51</td>
</tr>
<tr>
<td>Melamine and terephthaldehyde</td>
<td>LiCl/KCl-Eu</td>
<td>4 h @ 150 °C/2 h @ 400 °C/2 h @ 600 °C</td>
<td>332 – 586</td>
<td>0.14 – 0.31</td>
<td>84</td>
</tr>
<tr>
<td>Polymer monomers of melamine and terephthaldehyde</td>
<td>KCl/ZnCl$_2$</td>
<td>12 h @ 700 °C</td>
<td>426 – 1929</td>
<td>0.85</td>
<td>85</td>
</tr>
<tr>
<td>Pyromellitic dianhydride and p-phenylenediamine (or benzidine)</td>
<td>KCl/ZnCl$_2$-Eu</td>
<td>1 h @ 325 – 1000 °C</td>
<td>67 – 2607</td>
<td>0.12 – 3.12</td>
<td>71</td>
</tr>
<tr>
<td>1-butyl-1-methyl-pyrrolidinium bis ((trifluoromethyl)sulfonyl) Imide (Bmp-tfs)</td>
<td>KCl/ZnCl$_2$-Eu</td>
<td>2 h @ 850 °C</td>
<td>1056</td>
<td>0.86</td>
<td>86</td>
</tr>
<tr>
<td>Ionic liquids (1-ethyl-3-methylimidazolium dicyanamide)</td>
<td>NaCl/ZnCl$_2$</td>
<td>1000 °C</td>
<td>1410 – 1770</td>
<td>1.2 – 2.9</td>
<td>87</td>
</tr>
</tbody>
</table>
an oxidative pore formation.

Use of pure ZnCl$_2$ as solvent has been reported in the synthesis of triazine-based framework (CTF) by the condensation of, i.e., 1, 4-dicyanobenzene, which has a ordered crystalline structure and high SSA (around 800 m$^2$ g$^{-1}$),$^{30}$ In this system, the acid-base interaction between ZnCl$_2$ and the precursor ensures complete dissolution of the precursor and the formation of homogeneous solution. Further heating the CTF to higher temperatures beyond its stability limit in the ZnCl$_2$ salt melt results in the formation of completely amorphous carbonaceous polymer with SSA of 3300 m$^2$ g$^{-1}$ and pore volume of 2.4 cm$^3$ g$^{-1}$. This can be rationalized by the elimination of N content through breaking of C–N bonds by a fragmentation-recombination mechanism that releasing (CN)$_2$ at higher temperatures. After this report, a variety of other compounds have been used as precursors for the synthesis of porous carbons with rigid architecture and controllable porosity.$^{69, 70}$

ZnCl$_2$ is usually combined with alkali metal chloride for the production of porous carbon. For instance, ZnCl$_2$ forms eutectics with alkali metal chlorides with a lowest melting point of 230 °C for ZnCl$_2$/KCl. Fechler et al. have examined the carbonization of different ionic liquid precursors containing heteroatoms like B, N in the salt melt of ZnCl$_2$/ACl (A: Li, Na, K) at temperatures up to 1400 °C.$^{67}$ In these systems, the precursors can be completely solvated by the salt melt, thus enabling the formation of a homogeneous solution phase, for which porous carbon precipitates as a result of heating to high temperature by phase separation (Figure 9). The products with an irregular morphology demonstrate SSA of up to 2000 m$^2$ g$^{-1}$ and porosity of up to 2.75 cm$^3$ g$^{-1}$. The authors suggested that a “salt-templating” mechanism can account for the pore generation, which is solely dependent on the type of salt and not the precursor. Following this example, eutectic salt melts containing ZnCl$_2$ have been applied for the synthesis of highly porous carbons with heteroatoms doping and different structures including carbon layers from diverse precursors.$^{51, 71}$ Despite that the mechanism of pore formation is assumed to be quite physical, that is by “templating”, the formation of insoluble ZnO in the final product (which necessitate the use of HCl solution to wash the product) implies that ZnCl$_2$ may participate chemically in the carbonization process. Therefore, the exact role of salt could be rather complicated, as apparently ZnCl$_2$ is not chemically inert and plays an essential key role in pore generation in such system in comparison to the inert alkali metal chloride.

### 3.4 Precursors beyond sugar: heteroatom doping and structure control

The synthesis of porous carbons doped with N or S atoms has become of particular interest as they serve as actives sites for catalysis and enable more efficient energy storage. By using different precursors,$^{72−94}$ porous carbons doped with heteroatoms of N, B, S and P have been synthesized by the ionothermal process using precursors listed in Table 3. Unlike the cases discussed in section 3.1, the as-synthesized carbons inherit the C–N (or C–S, C–B) bonds from their precursors, and generally the fraction of such atoms drops with increasing the synthesis temperature (except for B, which forms stable B–C bonds). Among these heteroatom-doped carbons, N-doped ones have received the biggest attention. There are three types of C–N bonds found in N-doped carbons: pyridinic, pyrrolic, and graphitic C–N bonds. In section 3.1, most N atoms from nitrate salt are finally located at the edges of the layer which terminated the carbon sp$^2$ network in the form of pyridinic or pyrrolic C–N bonds, while use of N-contained precursors often results in the formation of large amount of graphitic nitrogen.

Whereas ionothermal process can produce carbons with controlled doping and high porosity from diverse precursors, the modulation of microstructure beyond porosity by this process has been challenging. To synthesize carbons with desired texture, some strategies applied in wet-chemistry synthesis have been transferred to ionothermal process and proved to the effective. In contrast to small molecular precursors, by using the “self-template” strategy the initial structure can be preserved for certain precursors after conversion to carbon by the ionothermal process. For instance, ionothermal derived carbon using cellulose fiber as precursor still preserves the tubular texture with similar diameter in addition to the high porosity.$^{44}$ This is because, cellulose fibers, as a typical polysaccharide, does not dissolve in the salt-melt during its carbonization, which is completely different from the carbonization of other salt-melt soluble molecules. In a quite similar fashion, porous precursors with well-defined pore structure, such as CTF and COF (covalent organic frameworks), have also been converted to highly porous carbon by the ionothermal process, in which the...
precursors serve as both carbon source and template for porosity. In fact, the ionothermal process has been applied for the templated synthesis of ceramic nanostructure by using hard templates like mesoporous silica that are robust again corrosion by salt melt.

In addition to porosity, structural chirality of a mesoporous catalyst can enable enantio-specific control of chemical reactions and are thus of particular interest for modern organic synthesis. The ionothermal process offers a facile route to chiral carbon synthesis with meanwhile high porosity. Fuchs et al. employed a chiral ionic liquid as the precursor and the eutectic NaCl/ZnCl\(_2\) as the salt medium. The reaction was performed at 500 °C in the salt melt and the chirality of the product was confirmed by circular dichroism (CD) spectroscopy, isothermal titration calorimetry (ITC), and chronoamperometry. The ionothermal process therefore can be a simple solution process to chiral carbon materials without the use of template.

3.5 Towards ionothermal synthesis in a “wet-chemistry” style

As the maxima operation temperature can be over 1000 °C, the ionothermal synthesis is usually performed in ceramic crucibles heated by electric furnaces. Unlike a wet-chemistry synthesis, the reaction is closed in a “black-box”, giving no access to observe or intervene in the progress of reaction. A recent report, however, showed that Schlenck-type system with quartz glass containers can be used for the ionothermal carbonization of a series of organic solutions in salt melt of pure ZnCl\(_2\). Carbonization process in such a system can be carried out in a wet-chemistry style by direct injection of the precursor solutions to the molten salt (Figure 10). This process, therefore, is more convenient and economic compared with heating in furnaces. The result demonstrates that all the organic solutions can be carbonized with high yield under the reaction temperature up to 550 °C. The products derived by such process showed high SSA of up to 1666 m\(^2\) g\(^{-1}\) with a pore volume of 2.8 cm\(^3\) g\(^{-1}\). In addition, use of precursors containing heteroatoms enables the production of doped carbons with high concentration of N or S of over 10% by weight. Depending on the type of precursors, the resultant carbons showed quite different morphologies, from particles, to fibers and layers. Among the different types of organic solution examined, layered carbons are only obtained by using ethylene glycol and glycol as precursors. The authors have also shown that the process can be easily extended for the synthesis of inorganic/carbon nanocomposite, as exemplified by the ZnS@C, Ni@C and Co@C.

The ionothermal process has been shown to be completely compatible with the system of wet-chemistry synthesis. However, such system has an obvious limitation, the low operation temperature, which, for most molecules, is too low to allow complete carbonization with a high graphitization degree. Further improvement of this system can be expected which can offer an economic and scalable ionothermal solution for synthesis of carbon and plenty of other inorganic materials.

4. Applications for electrocatalysis and energy storage

4.1 Electrocatalysis and organic catalysis

The high porosity combined with high level of heteroatom doping makes ionothermal carbons particularly suitable for...
heterogeneous catalysis, in which the density and the accessibility of the catalytic site determine the catalytic performance. Heteroatoms, like N, in sp² hybridized carbon have been proved to be the active sites for electrocatalysis in oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER). Therefore, the ionothermal carbon doped with N or S can be immediately applied for electrocatalytic reactions. As shown in work of Liu et al., ionothermal carbon nanosheets doped with N or S atoms both show high activity for the ORR in basic solutions (Figure 11). The samples demonstrate a small overpotential, high current density compared to commercial Pt/C catalyst, and a dominating 4-electron process at a wide potential range. In addition, the carbon based catalyst are robust against methanol crossover; in contrast commercial Pt/C is easily passivated (Figure 11f). In a more detailed analysis, it was found that a higher SSA with high fraction of mesopore is favorable for enhancing the catalytic activity for the ORR, while a high heteroatom concentration does not improve the catalytic performance. Indeed, the catalytic activity for the ORR is found in a recent report to be correlated with the detailed pore structure for chemically equivalent catalyst also derived from the ionothermal process. For the present case, the samples with higher content of N (or S) are all synthesized at lower temperatures; therefore they generally have much smaller conductivity (due to lower graphitization degree) and surface area, which could slow down electron transport and limit the accessibility of catalytic sites.

Besides serving as a catalyst itself, the porous ionothermal carbon can be a robust support for catalyst used in heterogeneous reactions. In a recent report by Zhang et al., the porous graphene-like carbon sheets derived from the eutectic KCl/ZnCl₂ salt have been applied as a support for Co₃O₄ particles for aerobic oxidation of alcohols and amines to aldehydes and imines. The high concentration of N in the carbon offers large amount of coordination sites that ensure stable and robust binding to the oxide particles. Examination of the catalytic performance showed that this catalyst afforded high conversion ratio in the aerobic oxidation of alcohols and amines.

4.2 Capacitive energy storage

Carbon based nanomaterials have been intensively explored for capacitive energy storage in electrochemical capacitors (or supercapacitors). The capacity depends on several factors, such as surface area, pore structure and the concentration of heteroatoms. The capacitance of pure carbon materials normally does not exceed 150 F g⁻¹, while heteroatoms can contribute to large pseudo-capacitance which can be over 200 F g⁻¹. In the case of ionothermal carbon derived from glucose, the highest recorded capacitance exceeds 300 F g⁻¹, as shown in Figure 12. In comparison to the ORR in which samples with higher SSA are generally better, in terms of capacitance the best samples have medium SSA (around 1000 m² g⁻¹), but high fraction of micropores and high content of N or S atoms. However, the results of a recent report indicated that that ultrahigh surface area could be beneficial for an ionothermal carbon doped with high content of nitrogen, which exhibited a maxima capacitance of 275.6 F g⁻¹ and retention of 50% at high scanning rate (2 V s⁻¹). The interplay of microporosity and heteroatom concentration in the capacitive energy storage has also been observed in carbon materials synthesized from other processes.

5. Summary

The ionothermal route has been shown to be a general yet economic and efficient process for the synthesis of functional carbon materials with controllable heteroatom doping and pore structure. Similar to the wet-chemistry synthesis, this process provides a liquid media for the carbonization of diverse molecular precursors in a dissolution-precipitation fashion, and enables the growth of both disordered and well-defined 2D carbon structures. Depending on the composition, the salt melt can be chemically inert, such as LiCl/KCl, which solely serves as the solvent; while oxysalt like nitrate, when used as additive, can direct a 2D growth of carbon structures and provide N atoms to the highly porous product. In comparison to the inert alkali metal chlorides, acidic chloride ZnCl₂ is quite active and efficient in pore generation for a plenty of precursors. On the other hand, the use of precursor molecules other than sugar not only gives access to a range of doped carbons, but also the creation of desired textures such as chirality. The high porosity together with easy heteroatom doping makes the ionothermal carbons attractive for applications such as electrocatalysis and capacitive energy storage.

The next step to advance ionothermal synthesis of carbon should focus on the enhancement of energy efficiency.
controllability and scalability of the process. Despite that experimental trial by using typical wet-chemistry glassware for ionothermal synthesis has been successful and apparently more energy efficient, the system still needs to be improved for high temperature operation and system reliability. Scalable production of high performance carbons orientated for energy-related applications by the ionothermal process will become realistic after overcoming these technical challenges.

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Notes and references

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