

# HYDROTHERMAL CARBON MATERIALS— ECONOMICAL, GREEN AND VALUABLE

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## Introduction

Sustainable Chemistry aspires to raise the value of less dangerous chemicals as well as it tries to produce high-quality products environmentally friendly from preferable renewable resources. It will be shown in this contribution that hydrothermal carbonization can turn into a model case for such a process: low value and widely available biomass can be converted into interesting carbon nanostructures using environmentally friendly steps. These low cost nanostructured carbon materials can then be designed for applications in crucial fields such as separation, energy conversion and catalysis. Besides controlling the chemistry of carbonization two other important prerequisites for the achievement of useful properties are the control over morphology both at nano- and macroscale and the control over functionality by chemical means in hydrothermal carbonization.

Obviously the technique of hydrothermal carbonization is not new [1], however it was only recently that this technique has been rediscovered by several working groups. [2,3,4] Since then, it became an important technique for the production of various carbonaceous materials and hybrids, usually applied at mild temperatures (< 200 °C) and in pure water inside closed recipients and under self generated pressure.

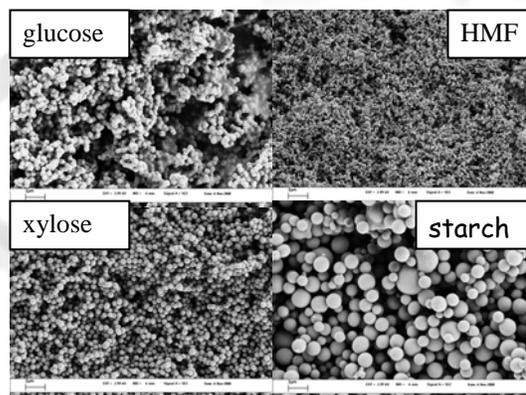
Here, we would like to summarize the latest advances in the synthesis of functional carbonaceous materials from different biomasses or biomass derived sources *via* the HTC process. In the first part we will focus on general aspects of hydrothermal carbonization, using either carbohydrates or complex bio-mass to control structure formation in the presence of various catalysts and/or templates. In the second part, we will focus on some of the most promising applications of the carbonaceous and hybrid materials obtained using hydrothermal carbonization.

## Results and Discussion

In order to gain some information about the fundamentals of the hydrothermal carbonization process, the hydrothermal carbonization of different carbohydrates and carbohydrate products was examined.[5,6] For instance, hydrothermal carbons synthesized from diverse biomass (glucose, xylose, maltose, sucrose, amylopectin, starch) and biomass derivatives (HMF and furfural) were treated under hydrothermal conditions at 180 °C and were analyzed with respect to their chemical and morphological structures by SEM, <sup>13</sup>C solid-state NMR and elemental analysis.

<sup>13</sup>C solid-state NMR also showed that starting from more complex, “real life” biomass instead of clean sugars does not change the outcome of the hydrothermal carbonization reaction, and remarkable similarities between the products of homologous series do occur, both with respect to morphology and local structural connectivity. Basically, the hydrothermal carbonization reaction takes place in three important steps: 1. dehydration of the carbohydrate to (hydroxymethyl) furfural; 2. polymerization towards polyfuranes 3. carbonization *via* further intermolecular dehydration.

The hydrothermal carbons obtained in the end from soluble, non-structural carbohydrates are micrometer sized, spherically shaped particle dispersions, containing a sp<sup>2</sup> hybridized backbone decorated with numerous polar oxygenated functionalities still remaining from the original carbohydrate. The presence of these surface groups offers the possibility of further functionalization and makes the materials more hydrophilic and well dispersible in water. The size of the final particles depends mainly on the carbonization time and precursor concentration inside the autoclave, as well as additives and stabilizers potentially to be added to the primary reaction recipe. Some SEM pictures obtained from various carbohydrate sources are given in Fig. 1. A typical yield for the carbon material is about 50% of the initial amount of carbohydrate



**Fig. 1** Scanning electron micrographs of various hydrothermal carbons obtained from different carbohydrate sources (scale bar 2µm)

The carbonaceous materials collected directly after hydrothermal carbonization possess only a small number of micropores and therefore a small surface area (as compared to activated carbons). For applications of these materials in fields such as catalysis, adsorption or energy storage, the presence of controlled porosity at the nanoscale is needed. This is why a variety of techniques were applied to increase the surface area. For instance, if hydrothermal carbonization of carbohydrates takes place in the presence of various templates or additives, interesting pore systems can be imprinted. [7,8,9,10] Figure 2 displays some morphologies of porous hydrothermal carbons obtained from carbohydrates.

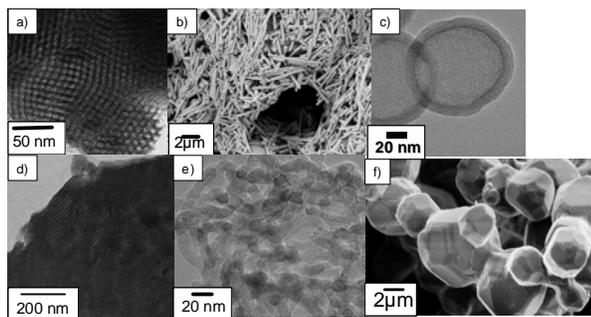


Fig. 2 a) SEM micrograph of a hydrothermal carbon replica of SBA 15 silica [8]; b) SEM of hydrothermal carbon nanotubes obtained using alumina membrane as template [9]; c) HR-TEM of hollow HTC spheres obtained from glucose in the presence of latex nanoparticles d)TEM showing an ordered mesoporous HTC using the self assembly of pluronics in the presence of fructose e) HR-TEM of a carbogel obtained using the hydrothermal treatment of glucose in the presence of albumin protein [15] f) SEM of HTC made via soft templating between F127 pluronic and fructose

Hydrothermal carbonization has been also intensively used for the production of various hybrids. Thus by performing this process in the presence of various metal salts [11] or preformed nanoparticles [12,13] nanocomposites with very interesting applications in extremely important areas can be produced.

Another gemstone in the portfolio of rational carbon synthesis is nitrogen-doped carbons. It was therefore straightforward to apply HTC by including sustainable nitrogen sources with appropriate co-reactivity to produce such materials. Thus we can either use naturally amino containing carbohydrates such as glucoseamine or chitosane or a mixture of carbohydrates and natural containing N compounds such as aminoacids or proteins to hydrothermally produce such desired materials under sustainable conditions. [14,15]

However one of the most appealing feature of hydrothermal carbonization is the fact that it represents an easy, green and scalable process allowing the production of various carbon and hybrid nanostructures with practical applications on a price base which is mostly well below any number of corresponding petrochemical processes. Even at this early stage, HTC materials have already found numerous applications in relevant fields of modern materials device manufacturing and the chemical industry such as catalysis, water purification, energy storage and CO<sub>2</sub> sequestration.

Thus, the hydrothermal carbonization process has been successfully as hard templates used to produce porous metal oxides hollow spheres which were not available via the classical sol-gel process. [11] Also using the hydrothermal carbonization in the presence of water soluble metal salts one can produce in situ nanocomposites with important applications in catalysis. For example Pd supported on hydrothermal carbon has been successfully used for the selective hydrogenation of phenol directly to cyclohexanone, a

process extremely important for the production of nylon.[16] Hydrothermal carbonization found also applications in electrochemistry where it has been successfully used to coat Si nanoparticles with C as a promising electrode in Li ion batteries [17,12,13] or in indirect carbon fuel cells.[18] Other applications of hydrothermal carbon imply water purification, e.g. removal of heavy metals from water as well as CO<sub>2</sub> capture. The nitrogen doped carbon materials have been successfully used as supercapacitors [19], adsorbents [20] or heterogenous catalysts in basic reactions, among which very important is the reaction of highly available CO<sub>2</sub> with propylene oxide resulting in a cyclic carbonate (propylene carbonate) which is a highly polar solvent, used as an electrolyte component for lithium batteries as well as an intermediate in polymer synthesis.[21]

### Conclusions

Although the HTC process has proved to be extremely successful in the production of many different distinctive structures rich in a variety of functional groups, there are still many aspects to be studied and considered in the future in order to facilitate the design of novel carbonaceous structures, with beneficial applications for our daily lives.

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