A Review of Hydrothermal Carbonization of Carbohydrates for Carbon Spheres Preparation

Rui Li\textsuperscript{1} and Abolghasem Shabbazi\textsuperscript{2,*}

\textit{1: Joint School of Nanoscience and Nanoengineering, North Carolina A & T State University, Greensboro, NC, United States}
\textit{2: Biological Engineering Program, Department of Natural Resources and Environmental Design, North Carolina A & T State University, 1601 East Market Street, Greensboro, NC 27411, United States}

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Carbon spheres have attracted a great deal of attention due to their applications as super capacitors, catalyst supports, and adsorbents. Carbon spheres can be prepared with controlled size and with oxygenated functional groups on the surface by the hydrothermal carbonization. The further processed products have a high surface area and high thermal stability. Among various methods for fabrication of carbon spheres, the hydrothermal carbonization is favored because of its mild operating conditions. In addition, hydrothermal carbonization can synthesize micro or nano scale carbon spheres environmentally friendly without employing organic solvents, surfactants, or catalysts. In this review, we present the effects of process parameters, structural characteristics of carbon spheres, possible formation mechanisms of carbon spheres, and applications in catalysis.

Keywords: Hydrothermal Carbonization (HTC); Carbon Spheres; Carbohydrates; Glucose; Process Parameters; HTC Mechanism; Applications of Carbon Spheres

1. Introduction

1.1 Carbon Spheres Preparation and Hydrothermal Carbonization

Carbon spheres have received growing research attention due to their structure [1-3], high electrical conductivity [4], and excellent chemical stability [5, 6], which exhibit potential applications in supercapacitors [7, 8], catalyst supports [9], and adsorbents [10]. Various approaches have been used to prepare carbon spheres, such as chemical vapor deposition [11, 12], the templating method [13, 14], pyrolysis of carbon sources [15, 16], and hydrothermal treatment [17]. Among the aforementioned approaches, the hydrothermal treatment method is more favorable because of mild operational conditions [18] and the controllable size of carbon spheres [19, 20]. Thus, the hydrothermal carbonization method provides an efficient and scalable route to synthesize carbon particles at low pressure and low temperature [21].

Hydrothermal carbonization (HTC) is a thermochemical conversion process carried out under mild operating conditions in a sub-critical water medium [22], while the critical point occurs at 374°C and 22.1 MPa in water [23]. During the HTC procedure, the solution of carbohydrate precursors is usually heated to 130-250 °C under self-
generated pressures [17]. HTC has several advantages: Firstly, drying wet feedstocks is avoided, which opens up a large variety of feedstocks with a high water content of 75-90 wt% [24]. Secondly, HTC operates in water at low reaction temperature. Thirdly, the products generally exhibit uniform chemical and structural properties. However, the products have almost no porosity, unless they were synthesized in the presence of a template or subjected to additional heat treatment at a higher temperature [25].

1.2 History of Hydrothermal Carbonization

The application of hydrothermal carbonization for carbon formation was first reported by the German chemist Friedrich Bergius, who was awarded the Nobel Prize in 1913 [26]. Over a long period of time, the hydrothermal process was mainly focused on producing aqueous products such as phenol, furan derivatives, and organic acids. So, the residence time of hydrothermal treatment was shortened to prevent further aromatization or polymerization. Because of multiple applications of carbon spherical particles, a renaissance of HTC of carbohydrates to synthesize carbon spheres at a low temperature gradually came back since 2001. Especially, it had attracted the interest of many researchers after 2006, since Dr. Markus Antonietti at the Max Planck Institute of Colloids and Interfaces (Germany) investigated more details of HTC [25].

1.3 Materials and Methods

Table 1 summarizes hydrothermal carbonization studies for carbon spheres formation between 2001 and 2014. Until now, simple monosaccharide and oligosaccharides have been effectively employed as HTC starting materials [27]. Extensive studies have been carried out on glucose as a model compound. Spherical carbon particles were prepared through either a direct hydrothermal process or a hydrothermal process followed by a carbonization process [28]. Experiments were carried out in an autoclave partly filled with the precursor solution. The autoclave was heated to a specific temperature for a given period of time. The reaction temperature and pressure were below the critical point of water. The obtained solid products were separated by centrifugation and washed with water and ethanol to remove residual byproducts, like levulinic acid.

<table>
<thead>
<tr>
<th>Products</th>
<th>Feedstock</th>
<th>Particle Size (μm)</th>
<th>HTC Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanospheres</td>
<td>Glucose</td>
<td>0.1-0.2</td>
<td>180°C for 4 h</td>
<td>[29]</td>
</tr>
<tr>
<td>Carbon spheres</td>
<td>Glucose</td>
<td>0.35</td>
<td>190°C for 4 h</td>
<td>[30]</td>
</tr>
<tr>
<td>Uniform carbon microspheres</td>
<td>Glucose, sucrose, and starch</td>
<td>0.4-6.0</td>
<td>170 to 240 °C</td>
<td>[31]</td>
</tr>
<tr>
<td>Carbon microspheres</td>
<td>Glucose</td>
<td>1-2</td>
<td>500°C for 12 h</td>
<td>[32]</td>
</tr>
<tr>
<td>Colloidal carbon spheres</td>
<td>Glucose</td>
<td>0.1-0.2</td>
<td>160°C for 6 h followed by 500°C for 4 h</td>
<td>[33]</td>
</tr>
<tr>
<td>Monodispersed hard carbon spheres</td>
<td>Sucrose</td>
<td>1-5</td>
<td>190°C for 5 h</td>
<td>[28]</td>
</tr>
<tr>
<td>Carbon microspheres</td>
<td>Starch</td>
<td>2</td>
<td>600°C for 12 h</td>
<td>[34]</td>
</tr>
</tbody>
</table>
2. Hydrothermal Carbonization Process

2.1 HTC Products of Glucose

The HTC products of glucose included an insoluble residue consisting of carbonaceous spherical particles, aqueous soluble products, and gaseous products [31]. The process water contained large quantities of aqueous soluble organic compounds [35]. Among them, a remarkable amount of hydroxymethylfurfural (HMF), levulinic acid, dihydroxyacetone, and formic acid were detected [20]. But phenol, phenol derivatives, other acids, and aldehydes were not found [36]. The gas phase consisted about 70-90% of CO₂, which derived from formate via decarboxylation [37]. Other gases were CO and H₂ [22].

Carbon spheres synthesized directly from carbohydrates at low temperatures possessed very low surface areas (<10 m²/g) with a small volume of micropores, which was common for hydrothermal carbons [38]. Highly disordered carbon spheres from glucose were hydrophilic amorphous carbons [8, 31], which had a polymer-like structure consisting of polyfuranic chains [33]. This polymer-like structure was formed through polymerization or aromatization of furan-like molecules [36]. So, the core of carbon spheres was composed of hydrophobic polyfuran compounds [20]. Carbon spheres had carbonyl [27] and carboxylic acid functional groups on the hydrophilic surface [39].

As an efficient way to enhance surface area, heat treatment may remove the functional groups from the surface of HTC carbons, and create some micropores. The surface area of glucose-derived HTC carbons after further heat treatment at 1000°C could reach 400 m²/g [28]. The morphology of HTC carbons did not change upon further heat treatment. But the surface appeared rougher because of micropore formation. If the heating temperature was too high, carbon spheres linked each other [40].

In terms of the carbon content, HTC of glucose increased the carbon content of colloid carbon spheres from 40 wt% to above 60 wt%, while the oxygen content was reduced [36]. After the further heat treatment, the carbon content increased from 60 wt% to above 80 wt%, while oxygen contents were correspondingly reduced [40].

2.2 Influence of Process Parameters

The size and the size distribution of colloidal carbon spheres prepared by HTC were influenced by processing temperature [41], reaction time, and the concentration of starting material [42].

2.2.1 Temperature

Colloidal carbon spheres were usually generated by HTC of glucose at a temperature of 170-260 °C. The minimum temperature for the hydrothermal carbon formation from glucose was 160°C, and hydrothermal carbonization did not take place below 160°C resulting in almost no solid residues [31]. At 180°C, HTC carbons formed were rich in carbonyl functionalities [41]. Increasing the HTC temperature led to hydrothermal carbons with a higher degree of aromatization, which was the normal tendency for a carbonization process. For example, hydrothermal carbon spheres, which were derived from HTC of 0.5 mol/L pure glucose solution for 4.5 h at different temperatures of 170, 180, 190, 210, and 230°C, had diameters of about 0.4, 0.44, 1.2, 1.2, 1.4 μm, respectively [31]. Above 280°C, only a very small fraction of carbon microspheres was generated, because the aliphatic carbon content decreased at temperatures higher than 260°C [43].
The processing temperature affected both the average diameter of carbonaceous particles and the size distribution. Higher temperature led to uniform particle diameter and a more homogeneous average size [41]. When the temperature was relatively low, glucose decomposed slowly. New nuclei may just form while the former nuclei already started carbonization, resulting in different growing time. So, under lower temperature, the size distribution was wider. When the temperature was relatively high, glucose can decompose completely very fast. All nuclei occurred at the same time, which led to a more homogeneous average size. But if the processing temperature was too high, formed microspheres had a risk to fuse together and become larger.

### 2.2.2 Residence Time

Exact residence time cannot be determined since reaction rates remained largely unknown, but typical published experimental residence time varied between 1 and 72 h [35]. A longer residence time led to higher reaction severity and less organic loss in the sugar solution. For instance, when HTC experiments were carried out at a constant concentration of 0.5 mol/L glucose and 160°C, as the residence time increased from 2 to 4, 6, 8, and 10 h, the diameters grew from 0.2 to 0.5, 0.8, 1.1, and 1.5 μm [42]. However, if the reaction time was too long, the produced carbon spheres fused, giving rise to particles with irregular shapes [30].

Dr. Titirici described in detail a conventional HTC process with a residence time [25]. When HTC experiments were carried out at a constant concentration of 10 wt% glucose and 180°C, during the first 2 h, no solid residues were observed, and glucose was dehydrated and decomposed into small soluble organic molecules. After 4 h, the color of the solution became dark orange suggesting that polymerization and aromatization occurred, called polymerization step. Past 5 h, the first solid precipitated out of the aqueous solution. After 8 h, a brown colloidal dispersion was formed. The black-brown solid formed spherically shaped particles of around 0.5 μm, aggregated together in 12 h. The growth process kept continuing, and the particle size increased to around 1.5 μm until all HMFs have been consumed.

### 2.2.3 Precursor Concentration

The size of carbon spheres increased with the elevated concentration of glucose solution within a certain concentration range [30]. When the concentration of glucose increased from 0.5 to 1 mol/L, the diameters grew from 1.2 to 1.4 μm, if HTC experiments were carried out at a constant temperature of 190°C and dwell time of 4.5 h [31]. However, when the concentration reached to a certain degree, the size turned to be constant. For example, at same reaction conditions, when the concentration of sugar increased from 1.5 to 3.0 mol/L, the average diameters in two samples were all 5 μm [28]. In addition, excessive concentration led to a larger particle size distribution. On one hand, a high concentration of carbon microspheres increased the probability of crosslinking. On the other hand, a higher concentration of glucose needed a longer time to dehydrate completely, which led to different formation time.

### 2.2.4 Carbohydrate Precursors

HTC had a wide range of possible sources such as carbohydrates (glucose, fructose, xylose, sucrose, cellulose, and starch) [31, 34], biomass [35], sewage sludge, animal manure, municipal solid waste [44], agricultural residues, and algae [24]. It’s difficult for HTC of biomass to form carbon spheres with regular morphology in a
uniform chemical structure compared to simple saccharides. For example, hydrothermal
carbonization of eucalyptus sawdust or barley straw at 250°C formed carbon
microspheres with the size of 1-10 μm from cellulose fraction of biomass. But these
carbon microspheres covered with particles retained the cellular appearance of raw
materials [45]. Therefore, carbon spheres from HTC of biomass were rarely used in
catalytic and electrode applications. So far, carbohydrates have been ideal starting
materials for preparing carbon spheres, because they were cheap and favored in the
dehydration process [46], and products had a uniform chemical structure. All materials
obtained from hexoses-based mono- (glucose, HMF), di- (maltose, sucrose), and
polysaccharides (amylopectin, starch) can be hydrolyzed to glucose units. Under similar
operational conditions, the diameters of carbon microspheres depended on the type of
saccharides used. The average diameter of carbon microspheres derived from different
carbohydrates had a sequence of sucrose > starch > glucose [31]. This variation was
related to the number of decomposed species generated from different saccharides, which
were obviously greater in the case of starch and sucrose due to their polysaccharide and
disaccharide nature, respectively [31]. Carbonaceous materials derived from pentose-
based carbohydrates showed morphological and chemical differences from hexose-based
ones [27]. Because furfural was the main dehydration product from pentose-based
saccharides, while HMF was the main dehydration product from hexoses-based
saccharides [40].

2.2.5 pH
The formation of acids was inevitable during the HTC, lowering the pH value to
~3 [31]. This acidic condition tended to increase the reaction rate in HTC, because the
hydronium ions generated from these acids catalyzed dehydration and further
polymerization of HMF [25]. A pH of 1.5 solution could increase glucose destruction
[47]. The addition of acid in the fructose solution caused high yields of HMF and furfural,
and decreased yields of pyruvaldehyde and lactic acid [48].

2.2.6 Pressure
Pressure had no significant effect on promoting HTC conversion, because the
HTC reaction occurred in the liquid phase. The resulting pressure in a close compartment
was higher than the saturated vapor pressure due to the formation of gases.

2.3 Possible HTC Mechanism of Glucose and Cellulose
The possible mechanism is schematically illustrated in Fig. 1. When glucose was
dissolved in water, it existed in three forms: an open chain, a pyranose ring, and a
furanose ring [49]. The levogluconan (1, 6-anhydro-β-D-glucopyranose) was produced by
the dehydration of glucose. Erythrose and glycolaldehyde were transformed from glucose
by retro-aldol condensation [50]. Glyceraldehyde was transformed from fructose,
isomerization of glucose, by retro-aldol condensation [51]. Dihydroxyacetone was
produced through reversible isomerization of glyceraldehydes, while both dehydrated to
form pyruvaldehyde [52]. Lactic acid was formed from pyruvaldehyde by benzilic acid
rearrangement [53]. Hydroxymethylfurfural (HMF) was produced from dehydration of
glucose [54, 55], and HMF hydrolysis produced levulinic acid and formic acid [56]. 1, 2,
4-benzenetriol was a decomposition product of HMF [57], while the 1, 2, 4-benzenetriol
could continue to polymerize with HMF or other intermediates [58].
Polymerization and condensation reactions may be induced by intermolecular dehydration or aldol condensation, forming soluble polymers [59]. At the same time, the aromatization of polymers took place. Aromatic clusters may be produced by the intermolecular dehydration of aromatized molecules generated in the decomposition or dehydration. The presence of reactive aldehyde and alcohol groups in HMF suggested that this compound may easily polymerize to give long-chain molecules [60]. HMF was also in situ “polymerized” to polymeric carbonaceous materials [61].

The growth of nucleated carbon particles may follow the LaMer model [62]. When the concentration of soluble polymers reached the critical supersaturation point, nucleation occurred upon segregating the formed polymer that was phased out of the aqueous solution. Then the nuclei grew outwards by diffusion of solutes present in the solution towards their surface. These species were linked to the surface of microspheres via reactive oxygen-containing functional groups [41]. This process was called carbonization [31]. When the growth stopped, carbon materials formed from glucose had a condensed furanic system consisting of a hydrophobic core and a hydrophilic shell embedded with levulinic acid [30].

During HTC of cellulose, most cellulosic substrates underwent intramolecular condensation, dehydration, and decarboxylation reactions; and were converted to aromatic network structures. A very limited degree of hydrolysis and consequential individual glucose formation most likely took place simultaneously at the cellulose-water interface [41], and then reactions followed the same reaction pathway as glucose during the hydrothermal treatment [31].

**Figure 1.** Schematic formation model for carbon spheres obtained from glucose and cellulose.
2.4 Applications of Hydrothermal Carbons

Carbon materials derived from HTC processes have been used as absorbents for removal of Cr(VI) [63] and Pb(II) ions in water [10], and materials for lithium-ion batteries [64-67]. Due to the good dispersion and functional groups prepared by the HTC method, carbon spheres can be ideal catalyst supports [68, 69].

One step HTC of the carbohydrate and metal solution can synthesize core-shell structure carbon spheres with hydrophobic metals as core and carbon as a shell. Silver cored carbon spheres were synthesized by HTC of HAuCl4 and glucose at 160-180 °C for 4-20 h [42]. Carbon spheres embedded with iron oxide nanoparticles, an excellent catalyst in the Fischer-Tropsch synthesis, was synthesized by HTC of glucose and iron nitrate [68]. During the hydrothermal treatment, iron nitrate was transformed to FeOOH, which was further reduced to iron oxide by hydrogen during the carbonization process. Carbon spheres embedded with palladium nanoparticles were synthesized by HTC of furfural and palladium acetylacetonate. During the HTC process, the palladium acetylacetonate was reduced to elemental metallic palladium nanoparticles [70].

Metal oxides hollow spheres could be synthesized in a one-pot synthesis via HTC of carbohydrate and metal salt. During this HTC process, a hydrophilic shell with -OH or C=O groups were prepared, and metal ions incorporated into the hydrophilic shell of carbon spheres. Hollow metal oxide spheres were obtained by calcining in air to remove encapsulated carbon. For example, the TiO2-hollow spheres were synthesized using carbon spheres as a template. Carbon spheres have -OH groups on their surface. The titanium source incorporated into the hydrophilic shell through the covalent –O-Ti bonding [71].

Inversely, carbon spheres with hollow structures can be made using metal as sacrificial templates. First, carbon spheres with the metal inside were made from hydrothermally treated carbohydrate and metal mixture. Then, the removal of metal resulted in hollow carbon spheres. For example, hollow carbon spheres were prepared from the HTC of glucose and Zn particles at 550°C for 8 h. The products were washed with HCl to remove Zn and ZnO inside. The hollow carbon spheres were about 1-2 μm in diameter, and the surface area was 207 m²/g [72].

3. CONCLUSIONS

Hydrothermal carbonization (HTC) of carbohydrates is shown as a green and sustainable technology to synthesize carbon micro or nano spheres, which have a core-shell structure with a highly hydrophobic and aromatic nucleus, and a hydrophilic shell containing oxygenated functional groups. HTC reactions take place in pure water at mild conditions with cheap precursors. The size and the size distribution of carbon spheres could be modulated by synthesis conditions such as the treatment temperature, the reaction time, the concentration of starting materials, and the type of precursors. Detailed mechanisms involved in HTC of glucose include hydrolysis, dehydration, polymerization, condensation, and aromatization. Although the mechanism of glucose HTC is almost confirmed, the mechanism for real biomass conversion is still under investigation, because of unknown contributions from lignin, protein, and lipid. The model is needed to predict the particle size and the size distribution from parameters such as temperature, residue time, precursor concentration, different saccharides, and solution filing degree. The new applications of carbon spheres are still being investigated.
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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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