We investigated the synthesis of carbonaceous spheres (CSs) via hydrothermal hydrolysis of aqueous solution of monosaccharides (glucose and fructose) in closed system. Different synthesis parameters such as temperature, reaction time, and sugar concentration are important for tuning the diameter of the CSs. In addition, control over the size of the CSs can be achieved using acetic acid as a size-determining agent.

The results show that important differences have been observed between both glucose and fructose derived CSs. For the production of well defined CSs the hydrothermal hydrolysis of fructose show lower reaction temperature and shorter reaction time if compared with hydrothermal hydrolysis of glucose. The particle sizes, however, are smaller when glucose is utilized as source of the CSs.

**Keywords:** Glucose; Fructose; Hydrothermal synthesis; Microstructure; Carbon materials

**INTRODUCTION**

Colloidal carbonaceous particles obtained from sugar are of great importance for scientists in various fields [1-2]. The pyrolytic treatment of carbohydrates such as glucose, sucrose, or starch mixed with water at mild temperature in an autoclave under autogenous pressure, produces water soluble organic compounds and a carbon rich solid product. This method termed as hydrothermal carbonization of sugar and it has been employed in material sciences for many years due to its advantages of being very cheap, mild and simple process to form carbonaceous materials with specific properties [3-5]. In 2001, Wang et al. [1] reported the synthesis of carbonaceous microspheres of a tuneable size (in the 0.25-5 μm range) through the hydrothermal carbonization of sucrose at 190 °C. Yao and co workers [5] investigated the mechanism of formation of carbonaceous microspheres in the course of the hydrothermal treatment of glucose. They concluded that during hydrothermal treatment, glucose loses water first (T=160 °C) through an intermolecular condensation reaction and that subsequently an aromatization (carbonization) process occurs.

Newly, the design and synthesis of carbonaceous materials with well define shape and size have attracted great interest due to the advantage of oxygen functionalities present on their outer surface layers [1, 3, 6]. A great deal of attention has also been focused on the hydrothermal carbonization of sugars in the existence of inorganic salts, which generates hybrid carbon/metal materials (C/Ag, C/Cu, C/Au, C/Pd, and C/Te) [2-3, 7]. Among the reported studies, some authors have taken advantage of oxygen functionalities present on the outer surface of the carbonaceous materials and used them as sacrificial templates to fabricate hollow spheres of inorganic materials [7-9]. In previous work, we have taken advantage of oxygen functionalities present on the outer surface of the CSs to fabricate inorganic hollow nanospheres by an advantageous sacrificial templating approach [10-13].

Though, to our knowledge, the mechanism of the hydrothermal carbonization of sugar is not fully comprehended at this stage and remains a challenge to material scientists, in an overview of the recent publications, there are few reports on the chemical transformations that occur when carbohydrate is treated - in closed system - in water [4-5, 14-15]. Generally, it was postulated that the formation of carbonaceous materials takes place through dehydration mechanism and subsequent nanoscale sequestering in aqueous solutions when heated at 180 or 135 °C in a pressurized vessel in case of glucose or fructose, respectively [4-5, 14-18]. We believe that the CSs out from monosaccharides are significant sacrificial templates for the synthesis of inorganic hollow materials. They are cheap and widely available precursors. Most important, the carbohydrate derived-CSs used in the sacrificial template approaches to fabricate hollow materials act as shape- and size-directing agents [10-13].

In this work, we have investigated the effects of various synthesis parameters such as temperature, reaction time, sugar concentration and addition of acetic acid on the formation of the CSs by the hydrothermal carbonization of glucose or fructose.

**EXPERIMENTAL**

Carbonaceous spheres (CSs) were obtained by the hydrothermal carbonization of the monosaccharides in closed system. In a typical synthesis for the production of CSs via the hydrothermal carbonization of glucose, 1900 mg of glucose in 100 mL deionized water (0.096 molL⁻¹) was transferred into 100 mL Teflon-lined stainless steel autoclave, followed by hydrothermal treatment of the solution at 180 °C for 24 h. While for the production of CSs via the hydrothermal carbonization of fructose, 2250 mg of fructose in 20
mL deionized water (0.625 molL⁻¹) was transferred into a 100 mL Teflon-lined stainless steel autoclave, followed by hydrothermal treatment of the solution at 135 °C for 6 h. After the hydrothermal hydrolysis reaction, the products were filtered off, washed with distilled water, and finally dried in a vacuum oven at 80 °C for 5 h. The impact of the synthetic conditions such as temperature, reaction time, sugar concentration and addition of acetic acid as a catalyst on the size and shape of the formed CSs by the hydrothermal carbonization of glucose or fructose were investigated. More precisely, to study the influence of each reagent on the morphology and the size of the final products, some crucial experimental conditions were systematically varied as shown in Table 1 and 2.

D(+)-Glucose monohydrate (C₆H₁₂O₆·H₂O) was obtained from Merck (Darmstadt, Germany). Fructose (C₆H₁₂O₆) was bought from dm, Germany. (CH₃COOH) was obtained from J. T. Baker (Deventer, Holland). All chemicals were analytical grade and employed without further purification. Distilled water (conductivity ~ 1.7 µS cm⁻¹) was used.

The carbonaceous materials were characterized by means of different experimental techniques. Details on the composition, morphology and properties of the CSs were obtained from infra red spectroscopy (IR), carbon hydrogen analysis (CH), scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen-sorption measurements.

RESULTS AND DISCUSSION

The hydrothermal hydrolysis reaction of the monosaccharides generates a solid residue, which is denoted as carbonaceous spheres (CSs), a name that depict both the nature of the product and the morphology. CSs with variable sizes were successfully obtained through economic and green one-step hydrothermal synthesis route utilizing aqueous solution of glucose or fructose in 100 mL Teflon-lined stainless steel autoclave. Scheme 1 is a schematic illustration of the facile green hydrothermal route.

The resulting CSs by applying glucose as a precursor under a variety of operational conditions (Table 1) have diameters in the range of 50 nm – 950 nm (Fig. 1). We observe that for temperatures in the range ≥200 °C as well as long reaction times >24 h, the CSs fuse, thereby produce particles with irregular shape (Fig. 2). The diameter of the CSs can be modulated by modifying glucose concentration or adding acetic acid as catalyst or reducing the time to 12 h. Variable concentrations of glucose were used. C1 stands for the initial glucose concentration of 960 mmolL⁻¹, C2, C4, C10 and C15 for 1/2, 1/4, 1/10 and 1/15 of C1, respectively; the catalyst used was 0.5 mL of acetic acid /100 mL of solution. We note that increasing glucose concentration, as well as adding of 0.5 mL acetic acid drive an increase in the mean diameter of the CSs due to the promotion of the rate of hydrothermal hydrolysis of glucose. In Figure 1. SEM microphotographs and size histograms of the CSs obtained by hydrothermal carbonization of glucose a)1-C1, b) 2-C2, c) 3-C4, d) 4-C10, e) 5-C15, f) 6-C10, g) 11-C10, h) 12-C2.

Figure 2. SEM microphotographs of the fused carbonaceous materials obtained by hydrothermal carbonization of glucose; samples a)7-C2, b) 8-C10, c) 9-C2, d) 10-C10.
addition, decreasing the time to 12 h reduces the average size of the resulting CSs.

### Table 1. Physical properties of the carbonaceous spheres resulting from the hydrothermal treatment of glucose

<table>
<thead>
<tr>
<th>Glucose sample code</th>
<th>c (molL⁻¹)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Sphere diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-C1</td>
<td>960</td>
<td>180</td>
<td>24</td>
<td>1000</td>
</tr>
<tr>
<td>2-C2</td>
<td>480</td>
<td>180</td>
<td>24</td>
<td>485</td>
</tr>
<tr>
<td>3-C4</td>
<td>240</td>
<td>180</td>
<td>24</td>
<td>375</td>
</tr>
<tr>
<td>4-C10</td>
<td>96</td>
<td>180</td>
<td>24</td>
<td>325</td>
</tr>
<tr>
<td>5-C15</td>
<td>64</td>
<td>180</td>
<td>24</td>
<td>55</td>
</tr>
<tr>
<td>6-C10/ catalyst</td>
<td>96</td>
<td>180</td>
<td>24</td>
<td>970</td>
</tr>
<tr>
<td>7-C2</td>
<td>480</td>
<td>180</td>
<td>36</td>
<td>shape abnormalities</td>
</tr>
<tr>
<td>8-C10</td>
<td>96</td>
<td>180</td>
<td>36</td>
<td>shape abnormalities</td>
</tr>
<tr>
<td>9-C2</td>
<td>480</td>
<td>200</td>
<td>24</td>
<td>shape abnormalities</td>
</tr>
<tr>
<td>10-C10</td>
<td>96</td>
<td>200</td>
<td>24</td>
<td>shape abnormalities</td>
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<tr>
<td>11-C10</td>
<td>96</td>
<td>180</td>
<td>12</td>
<td>220</td>
</tr>
<tr>
<td>12-C2</td>
<td>480</td>
<td>180</td>
<td>12</td>
<td>330</td>
</tr>
</tbody>
</table>

### Table 2. Physical properties of the carbonaceous spheres resulting from the hydrothermal treatment of fructose

<table>
<thead>
<tr>
<th>Fructose sample code</th>
<th>c (molL⁻¹)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Sphere average diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Fr1</td>
<td>2.5</td>
<td>150</td>
<td>6</td>
<td>shape abnormalities</td>
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<tr>
<td>2-Fr2</td>
<td>1.25</td>
<td>150</td>
<td>6</td>
<td>1150 nm</td>
</tr>
<tr>
<td>3-Fr2/catalyst</td>
<td>1.25</td>
<td>150</td>
<td>6</td>
<td>4.8 µm</td>
</tr>
<tr>
<td>4-Fr4</td>
<td>0.625</td>
<td>150</td>
<td>6</td>
<td>250 nm</td>
</tr>
<tr>
<td>5-Fr4/catalyst</td>
<td>0.625</td>
<td>150</td>
<td>6</td>
<td>2.2 µm</td>
</tr>
<tr>
<td>6-Fr4</td>
<td>0.625</td>
<td>135</td>
<td>6</td>
<td>200 nm</td>
</tr>
<tr>
<td>7-Fr4</td>
<td>0.625</td>
<td>135</td>
<td>24</td>
<td>shape abnormalities</td>
</tr>
<tr>
<td>8-Fr4</td>
<td>0.625</td>
<td>135</td>
<td>12</td>
<td>shape abnormalities</td>
</tr>
<tr>
<td>9-Fr16</td>
<td>0.313</td>
<td>150</td>
<td>6</td>
<td>150 nm</td>
</tr>
<tr>
<td>10-Fr16/catalyst</td>
<td>0.313</td>
<td>150</td>
<td>6</td>
<td>200 nm</td>
</tr>
</tbody>
</table>

**Figure 3.** SEM microphotographs of fused carbonaceous materials obtained by hydrothermal carbonization of fructose; samples a) 1-Fr1, b) 7-Fr4, c) 8-Fr4.

The resulting CSs by utilizing fructose as a precursor have diameters in the range of 150 nm – 4.8 µm (Table 2). We notice that for temperatures in the range ≥150 °C as well as long reaction times >6 h, the CSs fuse (Fig. 3). In addition, the optimal temperature to produce well defined CSs via the hydrothermal carbonization of fructose is in the range of 135-150 °C for 6 h, above and below which no results of interest will be observed. In this range the size is much smaller at lower temperature. The diameters of the CSs are influenced by reaction temperature, time, fructose concentration and catalyst. As evidence from Fig. 4 the size distributions of the CSs show that the average diameter becomes significantly smaller as a result of decreasing fructose concentration. Variable concentrations of fructose were used. Fr1 stands for the initial fructose concentration of 2.5 molL⁻¹, Fr2, Fr4, and Fr16 for 1/2, 1/4, and 1/16 of Fr1, respectively. Thus, at the same processing conditions the mean diameter follows the tendency: Fr16<Fr4<Fr2<Fr1. The addition 0.5 mL of acetic acid /20 mL of solution, as a catalyst, has a conspicuous effect on the growth of CSs as well. It catalyzes the carbonization reaction and promotes the rate of hydrothermal dehydration of fructose, hence, eventually leading to an increase in size.

Fig. 5a displays the IR spectra of glucose-derived CSs, the bands at 7110 and 1620 cm⁻¹, together with the band at 1513 cm⁻¹, attributed to C=O (carbonyl, quinone, carboxyl, or ester) and C-C vibrations, respectively, whilst the bands in the 1000–1450 cm⁻¹ region correspond to C-O (hydroxyl, ether, or ester) stretching. The bands at 875–750 cm⁻¹ are assigned to aromatic C-H out-of-plane bending vibrations, whereas the bands at approximately 2900 and 3000–1710 and 1620 cm⁻¹, together with the band at 1513 cm⁻¹, attributed to C=O (carbonyl, quinone, carboxyl, or ester) and C=C vibrations, respectively, whilst the bands in the 1000–1450 cm⁻¹ region correspond to C-O (hydroxyl, ether, or ester) stretching. The bands at 875–750 cm⁻¹ are assigned to aromatic C-H out-of-plane bending vibrations, whereas the bands at approximately 2900 and 3000–3700 cm⁻¹ correspond to stretching vibrations of aliphatic C-H and O-H (carboxyl or hydroxyl), respectively [2, 19-21]. The IR spectra of fructose-derived CSs, Fig. 5b, shows also the characteristic peaks related to O-functional groups. Comparative analysis of the IR spectra of the CSs and those of the glucose and fructose (Fig. S2) show that dehydration and aromatization processes take place during the hydrothermal carbonization. The CSs IR spectra contain some notable features ascribed to the appearance of the bands at 1620 and 3000 cm⁻¹.
One-pot hydrothermal synthesis of aqueous monosaccharides solutions

1513 cm⁻¹ which reveal the aromatization of the samples which is
typical for a carbonization process [2, 20].

The XRD patterns display the amorphous nature of the as-obtained
glucose- and fructose-derived CSs (Fig. 6).

The carbon hydrogen analysis (CH) of glucose and fructose and
their derived CSs samples, Table S1 and S2 in the Supporting
Information, respectively, show that the carbon content of the
glucose-derived CSs increases from approximately 36% to 64–66%
after the hydrothermal carbonization. Concomitantly, there is a
reduction in the oxygen and hydrogen contents. These variations in
the oxygen and hydrogen contents become greater as the reaction
temperature or time is increased or the catalyst is added which is
consistent with a carbonization process [7, 10]. In comparison to the
obtained glucose-derived CSs, we observe that fructose-derived CSs
display the same trends. However, they have approximately 4-5 %
lower carbon content and nearly 5 % greater oxygen content than
that in glucose-derived CSs. This likely is because the typical
carbonization time of fructose is 6 h which is shorter than the typical
carbonization time of glucose which is 24 h.

The N₂ adsorption isotherms (Fig. S3) reveal that the obtained CSs
have a poor porosity, the BET surface areas are 8 m²g⁻¹ for glucose-
derived CSs and 4 m²g⁻¹ for fructose-derived CSs. From that context,
we infer that the surface of fructose-derived CSs are less porous than
that of glucose samples and they are homogeneous CSs having a
smooth nonporous surface in accord with SEM micrographs.

**CONCLUSION**

In conclusion, functionalized CSs with size ranging between 55 nm
and 4.8 µm were produced by the hydrothermal carbonization of
monosaccharides (glucose and fructose). The results obtained from
SEM and carbon-hydrogen analysis (CH) combined with IR spectra
are evidence that, from a chemical point of view, the formed CSs
have a spherical morphology with a smooth surface, and are not pure
carbon but still carry hydrophilic oxygen functionalities. Consequently, they are suitable sacrificial templates for the
formation of various hollow inorganic particles.

The size distributions of the produced CSs shows some
trends such as, (i) the size of the CSs is directly proportional to the
sugar concentration; (ii) addition of acetic acid catalyzes the
hydrothermal reaction of the sugar and increases the rate of the sugar
hydrolysis, hence, increases the size of the CSs, (iii) shape
abnormalities occur when the reaction time is ≥24 h or ≥6 h for
glucose or fructose samples, respectively, while the other conditions
are typical procedures; (iv) analysis of the textural properties of the
glucose- and fructose-derived CSs shows that they have a poor
porosity, as evidence from N₂ adsorption isotherms. Moreover, the
results disclose important differences between glucose- and
fructose-derived CSs, such as the production of well-defined CSs.
via the hydrothermal hydrolysis of fructose show lower reaction temperature and shorter reaction time compared with hydrothermal hydrolysis of glucose. The particle sizes are smaller if glucose is used as source of the CSs. In addition, fructose-derived CSs are homogeneous spheres with smooth nonporous surfaces. Further work to investigate the chemical transformations that occur when monosaccharides is treated - in closed system - in water is in progress.

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BIOGRAPHY

Dr. Haitham Abdelaal received his PhD degree in February 2013 from Marburg University, Germany, under the direction of Prof. Bernd Harbrecht with a focus on materials chemistry in April 2013, he joined the Ceramics Laboratory, The National Research Center, Egypt, as a Research Scientist to work on the design of nanomaterials for the water treatment applications. Dr. Abdelaal is the recipient of the highly prestigious DAAD fellowship from German Academic exchange service (2009-2011).