

Starbon[®]: Preparation, applications and transition from laboratory curiosity to scalable product

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ABSTRACT

A number of years ago the Green Chemistry Centre of Excellence at York discovered new high surface area forms of polysaccharides. Further study of these materials has found that after controlled thermal treatment they exhibit remarkable thermal properties, which have enabled us to make an entirely new class of materials with properties ranging from starch-like to carbon-like (see figure 1).^[1] Trademarked Starbon[®] this novel family of mesoporous materials have surface functionalities ranging from hydrophilic to hydrophobic and utilizes the natural ability for polysaccharides to retain their organized structure during pyrolysis. The mesoporous Starbon[®] family now consists of a continuum of materials from a number of different polysaccharides from renewable sources.^[2]

This technology has been applied to a number of areas such as solid acid/base catalysis, catalyst supports, water purification, and chromatography and has recently been developed into a scalable commercial product.

Keywords: nanostructure, mesoporous, polysaccharides, catalysis, carbon

1 INTRODUCTION

The outstanding potential of mesoporous “carbonaceous” materials- in a wide range of applications that depend on mass transport of chemicals to the carbon surface- has led to the search for a methodology that grants the desired control over surface chemistry and distribution of pore sizes; especially one that minimizes formation of micropores, which are disadvantageous in applications such as chromatography^[3] and catalysis.^{[4],[5]}

One approach that achieves this goal is templating. In a typical procedure^[6] mesoporous silica is filled with a carbon precursor (e.g. sucrose), which is subsequently carbonized through a series of high temperature processes. The template is then removed using hydrofluoric acid or caustic soda. This method is multi-step, energy intensive, involves highly corrosive chemicals, and the resulting materials have a significant proportion of micropores. The functionality of materials produced by this method is also limited as techniques used for template removal can simultaneously solubilise carbons with high concentrations of oxygen-containing groups^[7].

The Green Chemistry Centre of Excellence at the University of York has developed a novel approach to the synthesis of mesoporous carbonaceous materials - utilizing the complex molecular architecture found in plant polysaccharides^[8]. Starch, for example, has a naturally, nano-channeled biopolymer structure which can be utilized as a template.

It was found that the heating of polysaccharides in water opens its internal structure allowing the polymer network to become accessible. Further treatment with *p*-toluenesulfonic acid and heating to different temperatures ranging from 200-1400 °C converts the expanded polysaccharide templates into stable, nanostructured, mesoporous, carbonaceous materials.

Variations in the temperature of polysaccharide carbonization help us to produce the family of novel nanostructured materials with readily controllable surface oxygen concentration, hydrophobicity and functionality which have the registered trademark Starbon[®] (see Figure 1).

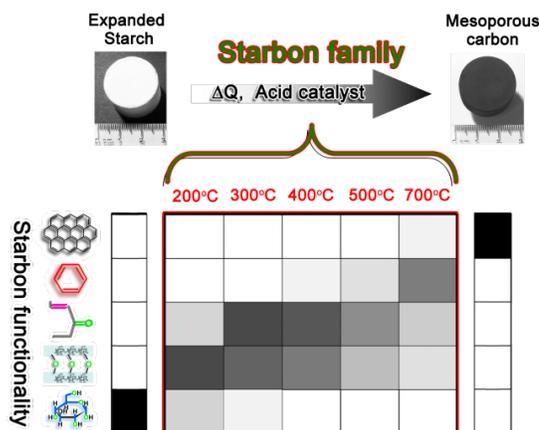


Figure 1: Influence of temperature of Starbon[®] preparation on surface functionality represented by shading.

This Starbon[®] technology also provides an entirely new, simpler and less wasteful route to mesoporous carbons. High mesoporosity and tunable surface functionality of Starbons[®] make them promising for a variety of applications including chromatography, catalysis, environmental remediation etc. and recently for making nanoparticles.

2 STARBON SYNTHESSES

The synthesis of Starbons[®] is based on using expanded polysaccharides as a precursor negating the need for a templating agent. This method utilizes, for example, the natural ability of the polysaccharide polymer chains within starch (amylose and amylopectin) to assemble themselves into organized, largely mesoporous structures. The method comprises of three key stages (Figure 2).

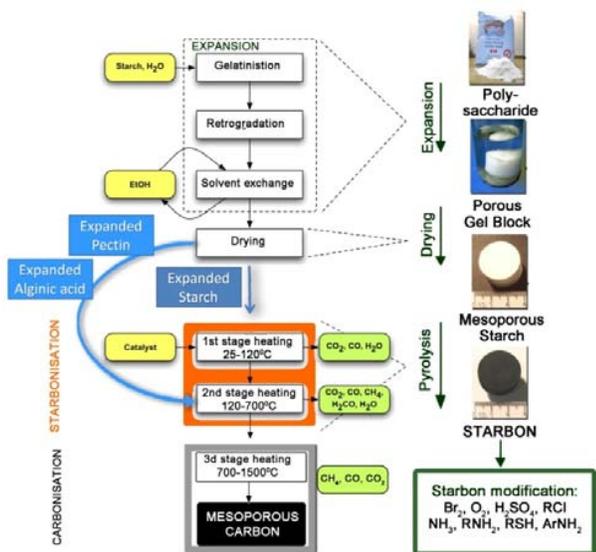


Figure 2: Method of Starbon[®] preparation.

Firstly, the polysaccharides are gelatinized by heating in water and subsequently cooled to 5 °C for one to two days to yield a porous gel block. The water in the block is then exchanged with ethanol, and oven dried to yield a predominantly mesoporous starch with a surface area of typically 180 m²g⁻¹.^[9] In the final stage, the mesoporous starch is doped with a catalytic amount of an organic acid (e.g. *p*-toluenesulfonic acid) and heated under vacuum.^[10]

Alternatively this method can be used for the polysaccharides pectin and alginic acid, which do not require a catalyst and can be converted into carbonaceous materials by heating alone.

A variety of mesoporous carbonaceous materials of controllable surface and bulk characteristics have been produced by heating to different temperatures ranging from 100-1400 °C. These can be in the form of a powder or in a stable monolith as shown in Figure 2.

3 STARBON PROPERTIES

3.1 Textural Properties

The porous structure of the Starbon[®] comes from the expanded starch, which negates the problem of micelle

collapse associated with micelle templated polymer- an alternative method for synthesizing mesoporous carbons. It also removes the need for the synthesis of mesoporous templates such as silica used to define structure.

The total pore volume and the average pore diameter in the mesoporous region remain essentially constant throughout the carbonization process. The average pore diameter in the mesoporous region is around 10 nm indicating a predominance of mesopores in the structure of Starbon[®].

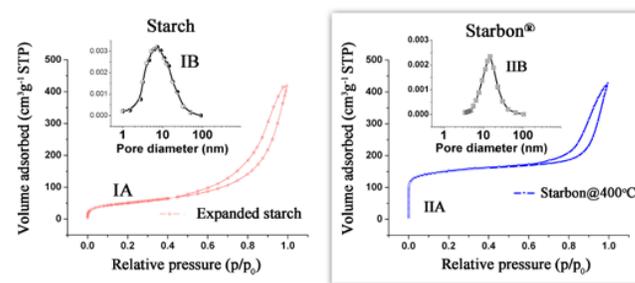


Figure 3: Textural properties of I) mesoporous expanded starch a) isotherm of adsorption; b) BJH desorption isotherm and II) Starbon[®] prepared at 400 °C a) isotherm of adsorption; b) BJH desorption isotherm.

Starbon[®] morphology is controlled by the inherent nature of the polysaccharide carbonized. Starch derived Starbon[®] has a spherical shape with particle sizes in the range of 5-15 μm. This is consistent with the size and shape of the original starch granules. Pectin and alginic acid derived Starbon[®] demonstrate a continuous phase network. Alginic acid derived materials are organized in a rod-like morphology into mesoscale sized domains, generating the large mesopore volumes.

The textural properties of Starbon[®] materials change with temperature. Although there is a substantial increase in the contribution of the microporous region to the total surface area with increased temperature, the actual volume that this corresponds to is small in comparison to the total mesoporous volume. Moreover, the level of mesoporosity (up to 98%) of Starbon[®] dramatically increases when it is made from pectin and alginic acid due to pore diameters changing from 7nm to 25nm. This emphasizes our control over the textural properties, first from temperature and secondly by choice of polysaccharide source.

These structural properties make Starbon[®] materials particularly suitable for applications such as catalysis, chromatography and adsorption of large organic molecules.

3.2 Surface functionality

The surface energy, E_{surface} , measured by the Dubinin-Astachov method illustrates an overall increase in E_{surface} as the preparation temperature rises. More starch-like properties are retained until about 150 °C, above which there is gradual change towards carbon like properties^[11].

X-ray photoelectron spectroscopy (XPS) further supports these observations indicating a near linear increase of carbon/oxygen ratio on the surface from 1.2 for expanded starch to 8.5 for Starbon[®] prepared at 800 °C (Table 1).

	Starbon [®] temperature preparation (°C)				
	Ex-st	100	300	600	800
C:O (EA)	1.2	1.3	3.4	7.53	8.6
C:O (XPS)	1.1	1.3	3.8	7.55	8.6
E _{DR}	7.4	6.9	17.7	24.4	25.8

Table 1: Carbon/oxygen ratio of Starbon[®] using elemental analysis and x-ray photoelectron spectroscopy.

Further characterization of Starbon[®] by TGA, ¹³C MAS NMR, DRIFT and XPS spectroscopy suggest that properties move to a graphite-like structure above 700 °C where there is a progressive increase in the hydrophobicity of the functional groups present. In the first step of starbonisation (150-200 °C), the CH₂OH groups in the starch condense to form ether groups. In the second step (200-300 °C) the CH₂OH groups in the starch form carbonyl groups conjugated with olefinic groups to form aliphatic and alkene/aromatic functions. In the third step (>300 °C), the aliphatic groups are almost completely converted to aromatic π -systems. Materials could also be prepared up to 1000 °C (showing extended graphitic character as confirmed by XPS analysis) with no decrease in the quality of the textural properties or alteration in the structural morphology.

4 STARBON[®] APPLICATIONS

Starbons[®] have tunable surface functionality and as such are highly desirable for many applications especially where diffusion of the species within the pore network is essential. Although the potential for Starbon[®] mesoporous carbons are vast due to their easily adaptable surface properties and array of pore structures, 3 key application areas have been identified in chromatography, catalysis and adsorption.

4.1 Chromatography

Starbon[®] materials derived from alginic acid are particularly attractive chromatographic stationary phase materials, as they present minimal micropore content; this avoids reduction in separation efficiency as a consequence of irreversible high energy analyte adsorption in sub 2 nm pores. It was found that these stationary phases are particularly efficient at separating the sugars glucose (mono-), sucrose (di-) and raffinose (trisaccharide). The

resultant Ion chromatograms had an excellent peak shape, and near baseline resolution.

4.2 Catalysis – esterification in water

Starbon[®] is an excellent support for heterogeneous catalysis where its unique and tunable surface characteristics are appropriate for many reactions including, unexpectedly, esterification reactions conducted in aqueous media. This is particularly important in biomass fermentation reactions, which produce a range of organic acids that can be utilized as platform molecules in applications such as the production of polymers and higher value intermediates. Esterification is one of the key upgrading steps for these acids. The fermentation process is carried out in aqueous media and the resulting aqueous broths require resource intensive separation steps before the acids can be upgraded. The new Starbon[®]- catalysts overcome this problem.

4.3 Adsorption

Low cost, naturally-derived adsorbents have great potential for use in both developed and developing countries for applications such as water purification and pollution control. The potential of porous carbonaceous materials for water purification requires a methodology that grants control over their surface chemistry, the distribution of pore sizes and as such makes Starbons[®] ideal candidate for such applications.

5 LABORATORY CURIOSITY TO SCALABLE PRODUCT

Recent EPSRC funding in collaboration with one of the UK's top contract chemical specialists has enabled this novel mesoporous material to be produced under economically favorable conditions.

Based on the market potential of these materials and the development work carried out at GCCE (to understand the properties and range of applications), the Starbon[®] technology is being spun out to make it available to the open market at industrial scale quantities. Since discovery a number of polysaccharides, whose properties are inherently unique, have been tested for suitability to become a Starbon[®] mesoporous carbon. However, recent work has focused on using a generic polysaccharide, which can be sourced from a variety of polysaccharides and is then treated to produce a product with homogenized predictable properties. This allows us to utilize an abundant polysaccharide source from a particular country, and realize its commercial potential immediately, while further developing and understanding its true characteristics. Starch and Alginic acid have been investigated predominantly as these are some of the most abundant land and marine base sources of polysaccharides.

6 CONCLUSION

The Green Chemistry Centre of Excellence has demonstrated an entirely new approach to the generation of nanostructures that is simple, utilizes natural materials, and avoids difficult and energy-intensive synthetic steps that are common in existing templating methods. Our approach utilizes the natural ability of plant polysaccharides to form nano-channels structures without the need of a templating agent and results in a new type of carbon-based materials with readily controllable physico-chemical properties.

It is well known that these materials are inert and have good thermal and electro-conductivities with potential applications in electrochemistry^[12], catalysis^[13], hydrogen storage^[14], and adsorption^[15], and are useful in certain types of supported catalysis. Furthermore, a new family of carbon-based mesoporous materials “Starbon[®]” with similar textural properties and progressively variable functionality can be synthesized by carbonization of expanded polysaccharides. The diversity of surface functional groups means that Starbon[®] can easily be modified. This, simultaneously with high surface area in the mesoporous region and mechanical stability, makes Starbon[®] particularly suitable for applications such as catalysis, chromatography and water purification within the range of preparation.

It was demonstrated that technology of Starbon[®] production is scalable and its manufacture is being developed. Possible future applications of these materials could be chiral chromatography (low temperature Starbon[®], up to 300 °C), fermentative catalysis, and specific adsorption of large organic molecules.

The broad scope of applications, combined with structural differences in native starch gives almost unlimited possibilities for this new and exciting class of materials.

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