

Thesis Review. Nanostructured carbohydrate-derived carbonaceous materials

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Objectives and novelty

Nanoporous carbon materials are widely used in industry as adsorbents or catalyst supports, whilst becoming increasingly critical to the developing fields of energy storage / generation or separation technologies. In this thesis, the combined use of carbohydrate hydrothermal carbonisation (HTC) and templating strategies is demonstrated as an efficient route to nanostructured carbonaceous materials. HTC is an aqueous-phase, low-temperature (e.g. 130 – 200 °C) carbonisation, which proceeds via dehydration / poly-condensation of carbon precursors (e.g. carbohydrates and their derivatives), allowing facile access to highly functional carbonaceous materials. Whilst possessing useful, modifiable surface functional groups (e.g. -OH and -C=O-containing moieties), materials synthesised via HTC typically present limited accessible surface area or pore volume. Therefore, this thesis focuses on the development of fabrication routes to HTC materials which present enhanced textural properties and well-defined porosity.

Results

In the first discussed synthesis, a combined hard templating / HTC route was investigated using a range of sacrificial inorganic templates (e.g. mesoporous silica beads and macroporous alumina membranes (AAO)). Via pore impregnation of mesoporous silica beads with a biomass-derived carbon source (e.g. 2-furaldehyde) and subsequent HTC at 180 °C, an inorganic / carbonaceous hybrid material was produced. Removal of the template component by acid etching revealed the replication of the silica into mesoporous carbonaceous spheres (particle size ~ 5 µm), representing the inverse morphological structure of the original inorganic body. Surface analysis (e.g. FTIR) indicated a material decorated with hydrophilic (oxygenated) functional groups. Further thermal treatment at increasingly elevated temperatures (e.g. at 350, 550,

750 °C) under inert atmosphere allowed manipulation of functionalities from polar hydrophilic to increasingly non-polar / hydrophobic structural motifs (e.g. extension of the aromatic / pseudo-graphitic nature), thus demonstrating a process capable of simultaneous control of nanostructure and surface / bulk chemistry.

As an extension of this approach, carbonaceous tubular nanostructures with controlled surface functionality were synthesised by the nanocasting of uniform, linear macropores of an AAO template with a diameter of 200 nm (Figure 1A and B for electron micrographs, Figure 1C for FTIR spectra). In this example, material porosity could be controlled, showing increasingly microporous tube wall features as post carbonisation temperature increased. Additionally, by taking advantage of modifiable surface groups, the introduction of useful polymeric moieties (i.e. grafting of thermoresponsive poly(N-isopropylacrylamide)) was also demonstrated, potentially enabling application of these interesting tubular structures in the fields of biotechnology (e.g. enzyme immobilization) and medicine (e.g. as drug micro-containers).

Complimentary to these hard templating routes, a combined HTC / soft templating route for the direct synthesis of ordered porous carbonaceous materials was also developed. After selection of structural directing agents and optimisation of synthesis composition, the F127 triblock copolymer (i.e. ethylene oxide (EO)₁₀₆ propylene oxide (PO)₇₀ ethylene oxide (EO)₁₀₆) / D-Fructose system was extensively studied. D-Fructose was found to be a useful carbon precursor as the HTC process could be performed at 130 °C, thus allowing access to stable micellar phase. Thermolytic template removal from the synthesised ordered copolymer / carbon composite yielded functional cuboctahedron single crystalline-like particles (~ 5 µm) with well ordered pore structure of a near perfect cubic *Im3m* symmetry (Figure 1A). N₂ sorption analysis revealed a

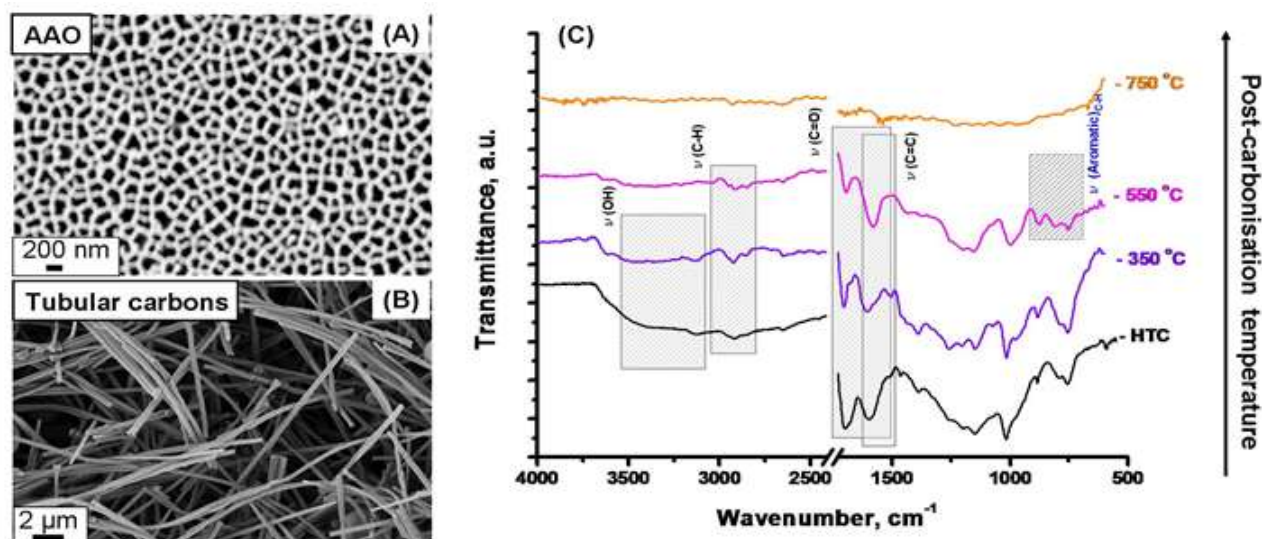


Figure 1. SEM micrographs of (A) template AAO and (B) synthesised tubular carbons. (C) FTIR spectra of tubular carbons post carbonised at different temperatures.

predominantly microporous carbonaceous material (i.e. Type I isotherm, $S_{\text{BET}} = 257 \text{ m}^2\text{g}^{-1}$, 79 % microporosity) possessing a pore size of ca. 0.9 nm (Figure 1C). The addition of a simple pore swelling additive (e.g. trimethylbenzene (TMB)) to this system was found to direct pore size into the mesopore size domain (i.e. Type IV isotherm, $S_{\text{BET}} = 116 \text{ m}^2\text{g}^{-1}$, 60 % mesoporosity) generating pore size of ca. 4 nm (Figure 1B and D). It is proposed that in both cases as HTC proceeds to generate a polyfuran-like network, the organised block copolymer micellar phase is essentially "templated", either via hydrogen bonding between hydrophilic poly(EO) moiety and the carbohydrate or via hydrophobic interaction between hydrophobic poly(PO) moiety and forming polyfuran-like network, whilst the additive TMB presumably interact with poly(PO) moieties, thus swelling the hydrophobic region expanding the micelle template size further into the mesopore range.

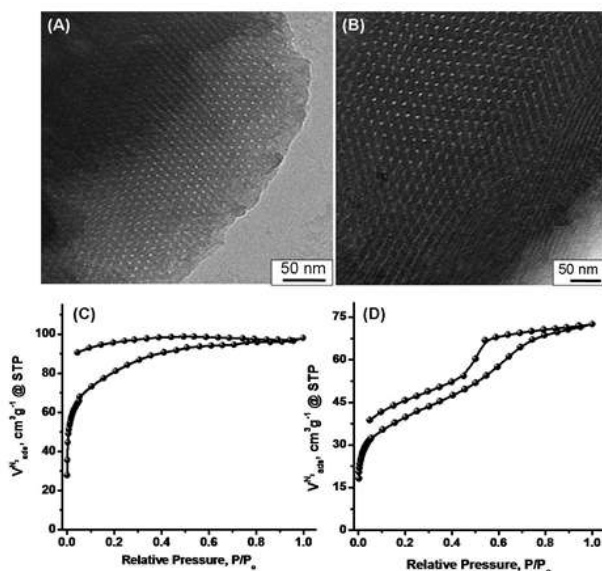


Figure 2. TEM micrographs of ordered porous carbonaceous materials synthesised (A) without and (B) with the addition of TMB. N₂ isotherms of the materials synthesised (C) without and (D) with the addition TMB.

Conclusions

The presented synthetic routes provide access to nanostructured carbonaceous materials with rich surface chemistry through a low-temperature, aqueous procedure using inexpensive and renewable carbon precursors. These carbonaceous materials are of potential interest as candidates in chromatography, electrochemistry or drug delivery. Here, ordered pore structuring potentially introduces the added properties such as linear electronic pathways desired for fast charge-discharge processes or facilitated encapsulation and release of drug molecules. This work represents an important contribution to the field of hydrothermal carbonisation demonstrating the possibility to introduce developed porosity and texture. As such the presented approaches are intended to lay the basis for the development of new high-value nanostructured carbonaceous materials with versatile applicability.

Related publications

- ¹S.Kubo, R.Demir-Cakan, L.Zhao, R.J.White, M-M.Titirici, "Porous Carbohydrate - Based Materials via Hard-Templating", *ChemSusChem*, 2010, 3, 188..
- ²S.Kubo, I.Tan, R.J.White, M.Antonietti, M-M.Titirici, "Template Synthesis of Carbonaceous Tubular Nanostructures with Tunable Surface Properties", *Chem. Mater.*, 2010, 22, 6590..
- ³S.Kubo, R.J.White, N.Yoshizawa, M.Antonietti, M-M.Titirici, "Ordered Carbohydrate - derived Porous Materials", *Chem. Mater.* 2011, 23, 4882..

Full thesis can be downloaded from http://opus.kobv.de/ubp/volltexte/2011/5315/pdf/ku_bo_diss.pdf