



New insights into the surface properties of hard-templated ordered mesoporous carbons

Xiaoan Li ^{a, b}, Farisa Forouzandeh ^a, Tobias Fürstenthaupt ^c, Dustin Banham ^{a, d}, Fangxia Feng ^a, Siyu Ye ^d, Daniel Y. Kwok ^b, Viola Birss ^{a, *}

^a Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada

^b Department of Mechanical and Manufacturing Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada

^c Microscopy and Imaging Facility, University of Calgary, Health Sciences Centre B129, 3330 Hospital Drive NW, Calgary, AB T2N 4N1, Canada

^d Ballard Power Systems, 9000 Glenlyon Parkway, Burnaby, BC V5J 5J8, Canada

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ABSTRACT

Although hard-templated ordered mesoporous carbons (OMCs) have been widely studied in the past decades, their surface properties, especially surface wettability, have not been investigated in detail. This study shows that as-synthesized hard-templated OMCs (sucrose- and anthracene-derived OMCs, *i.e.*, OMC-S and OMC-A, respectively, formed using the identical hexagonal mesoporous silica template) have very different surface characteristics, with OMC-S being significantly more hydrophobic than OMC-A. This is attributed to the presence of a thin, hydrophobic, microporous carbon shell layer surrounding the mesoporous core of the OMC-S particles, seen here for the first time by transmission electron microscope tomography and confirmed by the slower water uptake and slower electrochemical kinetics of OMC-S vs. OMC-A. At the same time, the mesopores within both OMC-S and OMC-A remain hydrophilic, as shown primarily by water vapor sorption measurements, due to the high density of surface oxygen groups inside the pores, as also confirmed by cyclic voltammetry. These oxygen groups are proposed to have been derived from C–O–Si bonds that formed at the carbon/silica interface during the carbonization process, leaving C–OH groups behind after removal of the silica template. These findings are relevant to a broad range of nanoporous carbon surfaces prepared with hard templates.

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1. Introduction

Ordered mesoporous carbons (OMCs) are of use in many applications primarily because of their high surface area as well as their controllable and ordered pore structures. Examples of their applications include as chromatographic supports, in lithium battery electrodes, biosensors, capacitors, adsorbents, catalyst supports, as fuel cell catalyst supports, *etc.* [1–4]. In recent years, a wide variety of OMC materials have been synthesized using various templating materials and a range of carbon precursors (carbon sources) [1–4].

The templates that have been used to produce the mesoporous structure of OMCs are normally classified into two types, soft and hard [2,3]. A soft template decomposes before the solidified carbon precursor is carbonized at high temperature, forming mesopores

[2]. A hard template (*e.g.*, mesoporous silica) can only be removed by dissolution after the precursor has been carbonized, leaving mesopores in the carbon structure [3,5]. Compared to the soft-template method, hard-template approaches employ a wider variety of carbon precursors [4,6–11], including carbohydrates and hydrocarbons [4,6,7], such as sucrose and anthracene. Of these, sucrose has been the most widely used for the synthesis of OMCs having a range of mesoporous structures [12–15].

The mesoporous structure of OMCs is defined by the framework of the mesoporous silica template. Hexagonal mesoporous silica (HMS) is a common example of a hard template that has a worm-hole structure, and thus the HMS-templated OMC structure has been described as consisting of interconnected carbon “worms” or “nanostings” [7,13,16]. In contrast, SBA-15, having tube-like mesopores, results in OMCs with an interconnected rod-like carbon framework (carbon “nanorods”) [3,6,17].

Despite the numerous past studies that have focused on the properties of OMCs (especially their porous structure) as well as their applications [1,3,13,16], these ubiquitous nanomaterials have

* Corresponding author.

E-mail address: birss@ucalgary.ca (V. Birss).

only rarely been examined in terms of their surface properties and wettability [18–20] and the specific role of the carbon precursors in influencing the OMC surface characteristics has not been studied as yet. Nevertheless, the general view is that the OMCs and related nanocarbon materials are hydrophobic in nature, although there is little data to support this supposition [1,21,22]. At the same time, it is known that surface wettability is critical to many of the applications of nanocarbons, with the optimization of their hydrophilic/hydrophobic character potentially taking their performance from very poor to excellent [23–30].

In this work, we used HMS as the hard template and sucrose (S) and anthracene (A) as the carbon precursors to synthesize OMCs, producing OMC-S and OMC-A, respectively (Supporting Information, Section S.1). These OMCs were also heat treated at 1500 °C under a N₂ atmosphere to increase their carbonaceous nature (named OMC-S-HT and OMC-A-HT, respectively), using the heat-treated OMCs as reference surfaces to aid in the understanding of the wettability data. The relative wettability of the OMCs was determined using contact angle kinetics (CAK) and water vapor sorption (WVS) methods [23], while their elemental content, porosity characteristics, and electrochemical behavior were also examined in order to understand their surface chemistry and wettability.

It is shown that both OMC-S and OMC-A possess highly hydrophilic internal mesopores, likely due to their high surface oxygen content (4–8 μmol/m²). As expected, heat treatment increases the degree of carbonization of the OMCs, removing most of the surface oxygen groups and lowering the hydrophilicity of the mesopore walls. Unexpectedly, however, the OMC-S particles were found to be significantly less hydrophilic than OMC-A, shown to be due to the presence of a newly discovered thin, microporous, and relatively hydrophobic carbon shell on the outer surface of the OMC-S particles, as seen by transmission electron microscope (TEM) tomography and confirmed by both slow water sorption rates and slow electrochemical kinetics. These differences are attributed to the differences in the conditions used during OMC synthesis, especially the different polarity of the carbon precursors.

Importantly, the methods developed in this work can be broadly applied to help understand the surface chemistry of any carbon powder. This makes the present work highly applicable to the nanoporous carbon community, particularly for those who are working on nanoporous carbon materials derived from hard templates.

2. Materials and methods

2.1. Preparation of OMCs

Sucrose- and anthracene-based ordered mesoporous carbons (OMC-S and OMC-A, respectively) were synthesized using hexagonal mesoporous silica (HMS) as the hard template, following the procedures reported previously [13,31,32]. Briefly, for the synthesis of OMC-S, 1 g of calcined HMS was mixed with an aqueous sucrose/H₂SO₄ solution (composed of 1.25 g of sucrose, 0.14 g of 98% H₂SO₄, and 5 g of water) and the mixture was dried at 100 °C for 6 h and then heated at 160 °C for another 6 h in air. The mixture was impregnated with another sucrose/H₂SO₄ aqueous solution (0.8 g of sucrose, 0.09 g of 98% H₂SO₄, and 5 g of water) and heated again, following the same procedures as before. The carbon precursor-silica composites were carbonized at 900 °C for 2 h in N₂, using a heating rate of 5 °C/min. OMC-S (~0.6 g, yield: ~30%) was obtained after removing the silica template with 2.5 wt % NaOH and drying at 120 °C for 12 h.

The synthesis procedures used for OMC-A were almost the same as those of OMC-S, except that the sucrose/H₂SO₄ aqueous solution

was replaced with an anthracene/H₂SO₄ acetone solution (0.44 g of anthracene dissolved in 50 mL of 0.14 M H₂SO₄/acetone). The impregnation of 1 g of HMS with the anthracene solution was repeated several times until the solution was fully consumed [13,31,32]. The carbon yield when anthracene was used in the synthesis of OMC-A was about 70%.

A portion of the synthesized OMC-S and OMC-A powders were treated at 1500 °C under a nitrogen atmosphere for 2 h at a heating rate of 5 °C/min. These heat-treated carbons were labelled as OMC-S-HT and OMC-A-HT, correspondingly.

2.2. Evaluation of OMC wettability

The relative wettability of the carbon samples was determined using contact angle kinetics (CAK) and water vapor sorption (WVS) measurements, following the procedures reported previously [23]. In brief, for the CAK experiments, the carbon powder samples (0.1 g for each) were pressed into pellets using a stainless steel die, and a 10 μL water droplet was released above the carbon pellets from a height of ~1 mm. The droplet behavior was recorded using a high speed camera (DRS Technologies) at a frame rate of 1000 fps and with a shutter time of 0.25 ms, giving the contact kinetics of water droplets on the pellets.

For the WVS experiments [23], 0.1 g of each carbon was placed into a porcelain crucible inside a sealed chamber having distilled water in its bottom (not contacting the specimen directly) at room temperature (23 ± 2 °C). The mass of the crucible plus the carbon sample was tracked as a function of time until it reached an equilibrium value. All of the OMC samples were placed in one chamber at the same time, allowing the accurate comparison of the relative wettability of the carbons.

2.3. Determination of OMC porosity

The specific surface area and pore properties of the carbon samples were determined by nitrogen adsorption/desorption analysis, with the data collected at 77 K using a Micromeritics Tristar 3020 analyzer (Department of Chemical and Petroleum Engineering, University of Calgary). Prior to the analysis, the samples were out-gassed in N₂ at 250 °C for 4 h [23].

2.4. Determination of electrochemical properties of OMCs

The surface properties of the OMCs were also determined using electrochemical methods in a 3-electrode cell containing N₂-saturated 0.5 M H₂SO₄, a Pt mesh counter electrode, and a reversible hydrogen (RHE) reference electrode [23,33]. The working electrode was prepared following the procedure reported previously [23]. 0.01 g of carbon powder and 0.1 g of 12 wt % H₂SO₄/ethanol solution were mixed in a vial, and then sonicated for 5 min, followed by the addition of 0.4 g of a 1 wt % Nafion/ethanol solution (obtained by diluting 5 wt % commercial Nafion solution with ethanol). After sonication for at least 1 h, 14 μL of the mixture (ink) was deposited onto the polished end of a glassy carbon (GC) rod (7 mm dia.), forming a carbon/H₂SO₄/Nafion film after the evaporation of ethanol in ~5 min. The cyclic voltammetry (CV) response of the film on the GC rod was then collected, as reported previously [23].

2.5. Elemental analysis and determination of surface morphology

The carbon, hydrogen and nitrogen content of the prepared carbons was determined using combustion analysis, while the inorganic residue (e.g., silica) content was determined using thermogravimetric analysis (TGA), as presented in our previous paper [23].

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