A novel porous carbon based on diatomaceous earth

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Received (in Cambridge, UK) 18th January 2006, Accepted 5th May 2006
First published as an Advance Article on the web 17th May 2006
DOI: 10.1039/b600708b

The production and characterisation of a carbon negative of diatomaceous earth which has a highly intricate and novel porous structure.

Due to the numerous applications of porous carbons as catalyst supports and current carriers in fuel cells,[1] there has been a great deal of interest in producing novel structures over a range of pore sizes. Mesoporous carbons with pore dimensions between 20 and 100 Å have been synthesised using a method involving templating with mesoporous silica materials[2,3] and several groups[4–6] have successfully incorporated metal centres into these structures to provide catalytic activity. The use of these mesoporous carbons in fuel cells has yet to be extensively tested and it is significant that the porous carbons utilised in most polymer electrolyte membrane (PEM) fuel cells have pore dimensions which are, at least, an order of magnitude larger than those which have been templated.[2–6]

Here we report a method for the production of a macroporous carbon utilising a similar templating technique which can be used to produce a carbon powder which has a higher surface area than the Vulcan XC-72 (250 $m^2\ g^{-1}$) used by E-Tek to manufacture catalysts for PEM fuel cells. Using this templating method has the advantage that the template can first be pressed into pellets or discs so that monoliths or membranes of the carbon structure could be produced. In addition, since the templating method is similar to that for the mesoporous structures, the same metal impregnation techniques can be used.

The basic method for production of templated carbons has been reported previously[5] but involves filling the void space of a silica template with sucrose which is then polymerised using sulfuric acid followed by carbonisation under a reducing atmosphere and finally dissolution of the silica using sodium hydroxide solution†. In this work the template which was used was commercial diatomaceous earth (Aldrich, Celatom FW80) which is imaged in Fig. 1. Diatomaceous earth is the mineralised exo-skeletons of diatoms, hence the agglomeration of the structures, and is the most abundant form of silica on earth. It has numerous applications as a filter agent, pesticide and was used by Alfred Nobel to absorb nitroglycerine to produce dynamite. As there are over 12 000 known diatom structures then there are potentially a huge variety of carbon structures which can be templated from them. Fig. 2 shows carbon structures from which the diatomaceous earth has been dissolved. During the impregnation of the sucrose, multiple washes with the sucrose solution were carried out. All of the samples shown in Fig. 2 received one sucrose impregnation.

The change in the pore architecture of the structures with repeated sucrose impregnation is shown in Table 1. Nitrogen adsorption experiments show that there is minimal microporosity while the mesopore volume is approximately 0.01 $cm^3\ g^{-1}$ with a mean mesopore diameter around 3.7–4 nm. The BET surface areas of the three samples rise from 180 $m^2\ g^{-1}$ after one sucrose impregnation to 312 $m^2\ g^{-1}$ after three sucrose impregnations. Mercury porosimetry shows a macropore volume ranging from 0.36 to 0.60 $cm^3\ g^{-1}$ and a mean macropore diameter of 2.5 μm which appears consistent with the SEM images.

Fig. 2. shows the carbon structure produced by one sucrose impregnation while Fig. 3(a) and (b) display SEM images of the structures generated by two and three sucrose impregnations.

Fig. 2 and 3 demonstrate conclusively that a negative structure of the diatomaceous earth is being produced in carbon. They clearly show the internal structure of the individual diatoms which initially is coated with carbon after one sucrose wash (Fig. 2(a) and (b)) but then becomes filled with carbon (Fig. 3(a) and (b)) as the amount of sucrose is increased. In addition, EDX analysis of the structures demonstrates the complete removal of the silica template by the sodium hydroxide dissolution step. Fig. 2(a) and 3(a) show

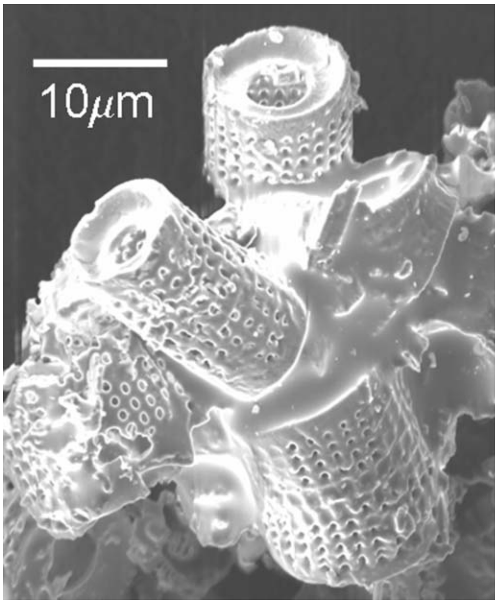

Fig. 1 SEM image of diatomaceous earth (Celatom FW80).

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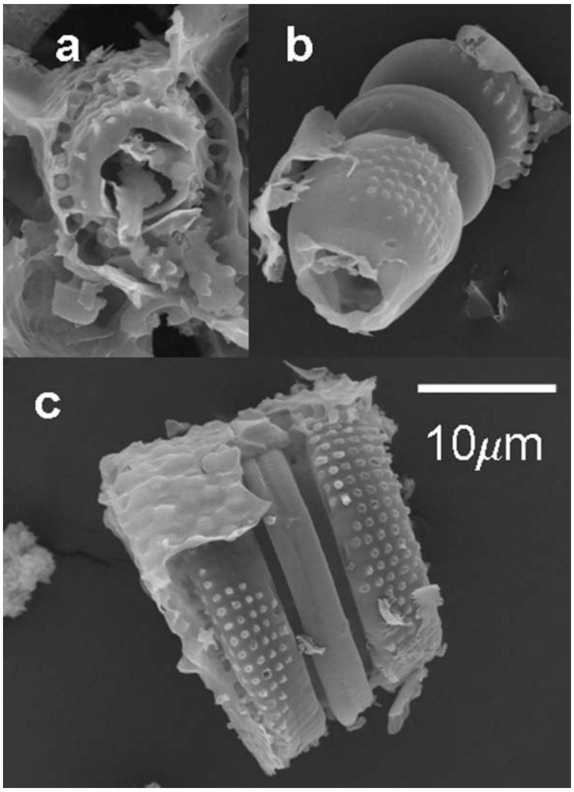

Fig. 2 SEM images of carbon negatives of diatomaceous earth fragments from which the silica has been dissolved (the scale bar is common to (a), (b) and (c)).

Table 1 Pore architectures of carbons formed from one, two and three sucrose impregnations. BET surface areas, meso/macropore pore volumes and diameters measured by N_2 adsorption and Hg porosimetry (total mass of sucrose added is per gram of Celatom)

Material (impregnations)	Carbon (1)	Carbon (2)	Carbon (3)
Total mass of sucrose added/g	0.64	1.01	1.25
BET surface area/m^2 g^{-1}	182	215	312
Mesopore volume/cm^3 g^{-1}	0.012	0.011	0.012
Mean mesopore diameter/nm	4.11	3.71	3.71
Macropore volume/cm^3 g^{-1}	0.458	0.603	0.362
Mean macropore diameter/μm	2.51	2.53	2.51

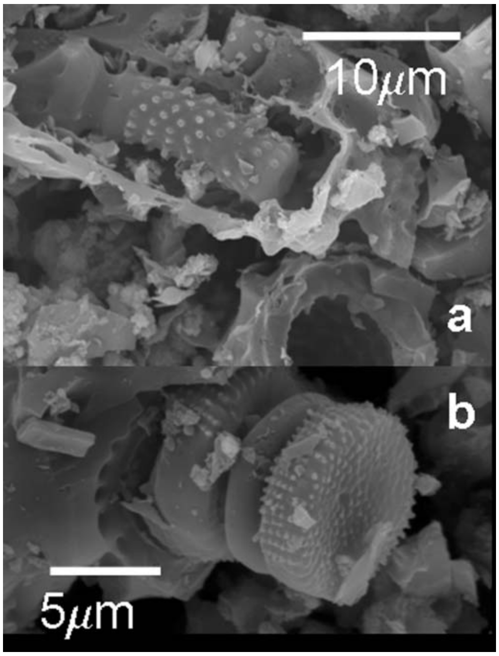

Fig. 3 Carbon structures produced by two (a) and three (b) sucrose treatments after silica dissolution.

an internal core of carbon which has formed down the centre of the diatom linked to an external skin, which has been deposited on the external surface, by carbon rods which have grown in the small pores in the wall of the diatom. The void space between the inner core and the outer skin is produced when the template is removed.

These structures do not have the same ordered structure of, for example, the silica which is grown around latex spheres to produce macroporous silica.[7] However, diatomaceous earth is an extremely abundant and cheap material and sucrose is also an inexpensive starting material. The synthesis technique is a simple process and it would be straightforward to produce a physical (or chemically synthesised) mixture of diatomaceous earth with either mesoporous silica such as MCM-48 or microporous zeolites.[8] This mixed template would enable the production of a tailored, hierarchically porous, carbon material into which catalytically active centres such as platinum could be readily incorporated using the techniques already developed. Alternatively, other natural structures such as pollen grains could be used to template porous carbons as in the work by Mann *et al.*[9] in which inorganic calcium and silica structures are templated from mixed flower pollen.

In summary, we have demonstrated a straightforward and economical method or producing high surface area carbon structures which could be readily applied to the manufacture of porous carbon membranes, monoliths, powders or hierarchically porous carbon materials.

The authors wish to acknowledge CONACYT-Mexico for funding Mrs B. E. Graniel-Garcia's PhD program at the University of Manchester.

Notes and references

† Carbon analogues of the diatomaceous earth were prepared by soaking Celatom FW80 (Aldrich) in a solution of sucrose and sulfuric acid. The solid was then heated for 12 h at 100 °C followed by 6 h at 160 °C which causes the acid to cross-link the sucrose. Further sucrose impregnations (1–3 impregnations) were carried out using masses of sucrose shown in Table 1. The sucrose was then carbonised under vacuum at 900 °C for 4 h. Dissolution of the silica template was carried out using 1 M NaOH in a 50 : 50 water–ethanol mixture at 90 °C under reflux.

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