Design and Synthesis of Mesoporous Silica Templates for a Novel Free-Standing Graphene Foam

by Anna E. Stewart

Free standing graphene foam materials that follow a triply periodic minimal surface (TPMS) are highly desired materials of both fundamental and practical importance. A three-dimensional carbon-based material of monolayer thickness whose underlying structure lies on a TPMS is a member of the class of hypothetical carbon allotropes known as schwarzites. A true schwarzite has not been synthesized despite their predicted low energies compared to other fullerenes. If achieved, such materials would have large pore volumes and surface areas and no edges, making them key candidates for gas storage and electrochemical applications. In this work, we have designed a novel synthesis strategy to achieve two different types of yet undescribed schwarzite-like materials: bilayer and interpenetrating. Both incorporate a hard-templating route; the chosen templates must carry the gyroid topology (cubic Ia-3d space group) and optimized pore-to-wall ratio. In this work we focus on the optimization of the structure of suitable template materials by varying hydrothermal time and temperature.

Introduction

A triply periodic minimal surface (TPMS) material has negative Gaussian curvature and a net curvature of 0 at every point. Such structures therefore complement flat and positively curved structures such as polyhedra, tubes, and sheets[1]. A three-dimensional carbon-based material whose structure is atomistically thin and lies on a TPMS is a member of the class of carbon allotropes called schwarzites[2]. These materials have not yet been synthesized but have been theorized to exist since 1991[3,4,5,6]. Schwarzites and schwarzite-like materials (e.g., unbalanced TPMS carbons or "carbon foams," continuous minimal surface structures with no edges) would have interesting properties such as ballistic electrical conductivity (perhaps at room temperature) combined with a fully free-standing structure with minimal defects. These properties, in addition to their large pore volumes and high surface areas, make such materials key candidates for gas and ion storage applications.

There are a variety of ways to synthesize free-standing graphene foam materials. The method proposed herein is a hard-templating route, wherein a monolayer of carbon is placed on a sacrificial template whose optimized pore structure follows a TPMS. This route is well-explored for non-TPMS substrates such as microbeads and clays,[7,8] and even for some TPMS-carrying templates such as zeolites[9]. However, the latter case (leading to zeolite-templated carbons, ZTCs) has never led to a schwarzite, owing to the narrow confinement of the carbon precursor which restricts the formation of connected graphene networks without edges[10].

Therefore, the choice of the template is crucially important to obtaining a schwarzite-like material. In this work, we explore templates that follow the gyroid TPMS (i.e., the Schoen G surface) which exhibits the cubic Ia-3d space group (**Figure 1**). In actuality, such templates contain two interpenetrating chiral channels that are separated by a gyroid surface. Several mesoporous silicate materials (themselves templated by an organic surfactant) lend themselves to this structure. Specifically, two mesoporous silicate materials (KIT-6 and MCM-48) have been identified as having an open, three-dimensional porosity with Ia-3d symmetry and a gyroid-like structure (with finite wall thickness). While both templates have a similar minimum wall thickness, KIT-6 typically has slightly larger pores than MCM-48.

We propose herein that KIT-6 could be used to produce two novel "schwarzite-like" materials upon templating: interpenetrating and bilayer. An interpenetrating schwarzite-like material would result if a KIT-6 variant with thick walls and a pore-to-wall ratio equal to ~1 would be used, as shown in **Figure 2a**. A bilayer schwarzite would result if a template with a maximum pore-to-wall ratio would be used, as shown in **Figure 2b**. Both materials are predicted to exhibit similar material and chemical properties; however, a bilayer schwarzite-like material will exhibit more similar porosity to a "true" schwarzite than an interpenetrating one. One the other hand, an interpenetrating schwarzite could have electrical properties closer to single-layer graphene. Neither type of schwarzite-like carbon foam has ever been reported; this paper will focus on optimizing KIT-6 for both types of schwarzite-like materials.

In both cases, after a monolayer of carbon is placed at the surface of the template, the silica template would then be removed via an acid wash (**Figure 3**). A monolayer or bilayer of carbon lying near the TPMS surface would remain, containing effectively no edges and resembling a schwarzite. Deposition conditions to achieve such a material are well-explored for other systems[8] and lay a clear path forward for future work.

Experimental Section

Synthesis: The hydrothermal synthesis of KIT-6 was performed following the procedure described by Ryoo and coworkers[11]. The triblock co-polymer Pluronic P123 was used as the surfactant and n-butanol (BuOH) as a structure-directing agent.

First, 7.9 g of aqueous HCl (35%, Aldrich) was added to 144 g of distilled water. Then, 4.0 g of P123 (average Mn ~5,800, Sigma Aldrich) was dissolved in this aqueous mixture at 35 °C for 24 h; 4.0 g of BuOH (99.4%, Aldrich) was then added, and mixed for 1 h at 35 °C. Finally, 8.6 g of tetraethyl orthosilicate (98%, Acros) was added and stirred for 24 h at 35 °C. The mixture was then aged at a specified temperature (35-80 °C) for a specified amount of time (24-72 h). The precipitate was filtered immediately, dried for 24 h at 100 °C, subjected to an ethanol/HCl wash, and then calcined at 550 °C under flowing air to obtain a surfactant-free product.

Characterization: Powder X-ray diffraction (XRD) was measured with Cu $K_{\alpha 1,2}$ radiation (λ=1.54 Å), generated at 40 kV and 40 mA, in Bragg-Brentano geometry, using a theta-theta diffractometer (D8 Advance, Bruker Corp.). The powder was mounted in the recessed well of a frontload sample holder; a 0.1 mm divergence slit, 0.5 mm anti-scatter screen, and 3 mm anti-scatter detector slit were used. Nitrogen adsorption/desorption isotherms were measured at 77 K between 10-3and 100 kPa using an automated volumetric instrument (3Flex, Micromeritics Instrument Corp.). Samples were prepared by degassing at 200 °C overnight under active vacuum. Pore-size distributions were calculated by fitting the data to a Barrett-Joyner-Halenda (BJH) model using the adsorption branch.

Results and Discussion

The long-range pore-to-pore ordering of the KIT-6 materials was confirmed by XRD analysis (**Figure 4**), with each material exhibiting an intense primary reflection at 2θ = 0.85°-1.1°. This peak

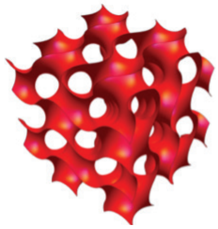

FIGURE 1
Gyroid surface
Schoen's "G surface", an infinite triply periodic minimal surface with high symmetry.

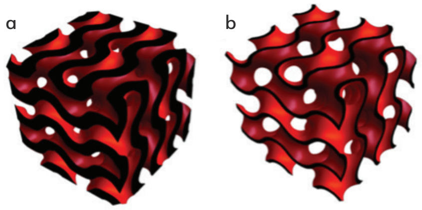

FIGURE 2
Templates for schwarzite-like materials
Two new schwarzite-like materials are envisioned, requiring specific templates: (a) a 1:1 pore-to-wall ratio template with thick walls for an interpenetrating schwarzite-like material and (b) a maximum pore-to-wall ratio template with thin walls for a bilayer schwarzite-like material.

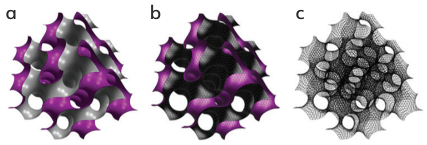

FIGURE 3
Synthesis of a free-standing graphene foam
The hard-templating synthesis route, showing three steps: (a) template design/synthesis, (b) graphene deposition on the template, and (c) dissolution of the template to produce a free-standing graphene foam.

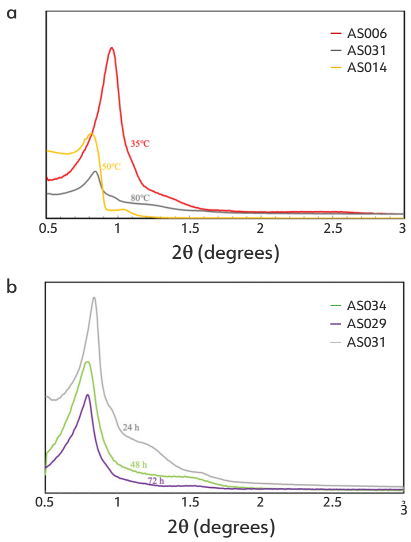

FIGURE 4

XRD analysis of KIT-6

Two series of KIT-6 materials were prepared: (a) by varying the hydrothermal temperature (hydrothermal time help constant at 24 hours) and (b) by varying the hydrothermal hold time (hydrothermal temperature held constant at 80°C).

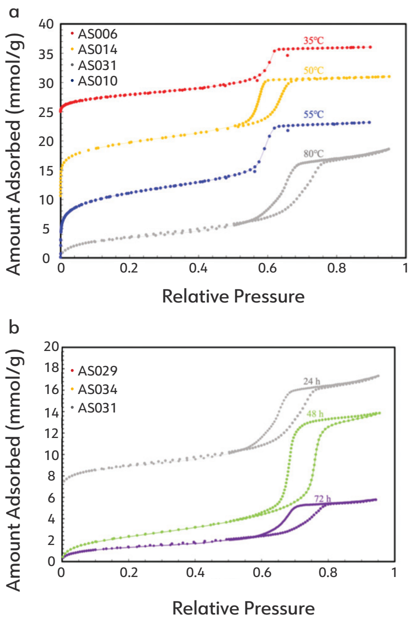

FIGURE 5

Nitrogen adsorption analysis of KIT-6

Two series of KIT-6 materials were prepared: (a) by varying the hydrothermal temperature and (b) by varying the hydrothermal time.

was indexed as the (211) reflection of the srs net (exhibiting Ia-3d symmetry). In the hydrothermal temperature series, an increase in temperature corresponded to a shift in the (211) reflection to lower angle (larger unit cell). Likewise, in the hydrothermal treatment time series, the (211) reflection shifted to lower angle (larger unit cell) with increasing hydrothermal time.

Using Bragg's law, the angle of the (211) reflection was used to calculate the cubic lattice parameter, a, of each material (**Table 1**). Based on the geometry of the srs net, the lattice constant was converted into the unit cell diagonal by multiplication by √3 and then into the pore-to-pore repeat distance by dividing by 4. A single pore-to-pore repeat distance is equal to the sum of the average thickness of one wall and the average width of one pore.

The classification of the KIT-6 materials as ordered mesoporous materials was determined by nitrogen adsorption analysis (**Figure 5**). All of the materials show a classic Type IV isotherm with a narrow hysteresis loop centered at P/P_0 = 0.5-0.65 indicating the presence of a narrow distribution of mesopores and few or no micropores or macropores. The pore-size distributions were estimated using the BJH model (**Figure 6**) and the primary pore width was tabulated (**Table 1**).

The average wall thickness of each material was calculated by subtraction of the BJH pore width from the XRD pore-to-pore repeat distance (**Table 1**). This feature could then be used to directly calculate the pore-to-wall ratio for each sample, the figure of merit for designing effective templates for the synthesis of both interpenetrating and bilayer schwarzite-like materials. AS014 is revealed as an excellent candidate for an interpenetrating schwarzite-like material, having a pore-to-wall ratio of 1.0. Meanwhile, AS029 is an excellent candidate for a bilayer schwarzite-like material, having a pore-to-wall ratio of 3.6.

Conclusions

Two novel types of schwarzite-like solids that are obtainable by the hard-templating approach (graphene deposition and then removal of the template via acid dissolution) are proposed. The ideal templates for such materials have been designed and synthesized. Variants of KIT-6 with close to a 1:1 pore-to-wall ratio are ideal candidates for the synthesis of an interpenetrating schwarzite-like material. KIT-6 was also optimized for large pore-to-wall ratio and minimal wall thickness, as an ideal candidate for the synthesis of a bilayer schwarzite-like material. Control over pore size, wall thickness, and unit cell size was demonstrated herein through variations in hydrothermal temperature and time, though future efforts to improve pore size homogeneity will be needed. Al-doping will also be explored in future work[12], permitting optimization of the graphene deposition step. Electrical conductivity will also be tested once carbon has been deposited on the templates.

In summary, both types of proposed novel mesoporous carbon materials would likely exhibit little or no edge character, high electrical conductivity, and large pore volume and surface area. This, coupled with the fact that their synthesis is relatively cheap and the materials required are widely available, makes them promising candidates for numerous energy storage applications.

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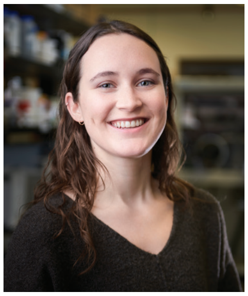
About the Author



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	T (°C)	Time (h)	a (Å)	W_{wall} (Å)	W_{pore} (Å)	R
AS028	80	24	255	36.5	74	2.0
AS031	80	24	252	38.2	71	1.9
AS034	80	48	268	29.2	87	3.0
AS029	80	72	251	23.6	85	3.6

	T (°C)	Time (h)	a (Å)	d_{211} (Å)	W_{BJH} (Å)	R
AS006	35	24	223	45.5	51	1.1
AS014	50	24	255	56.5	54	1.0
AS010	55	24	261	60.8	52	0.9
AS028	80	24	255	36.5	74	2.0
AS031	80	24	252	38.2	71	1.9

TABLE 1

Summary of KIT-6 materials properties

The materials properties of two series of KIT-6 materials: unit cell parameter, a, wall width, wwall, pore width, wpore, and pore-to-wall ratio, R.

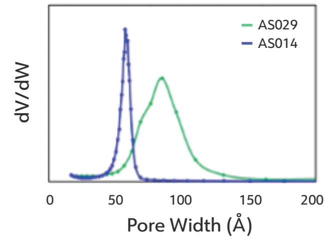

FIGURE 6

Pore-size distributions of optimal KIT-6 templates

Pore-size distributions of optimal templates for the production of an interpenetrating schwarzite-like material (AS014) and a bi-layer-type schwarzite-like material (AS029). Efforts to reduce the width of the pore-size distribution of AS029 are an important aspect of future work.