# Registered growth of mesoporous silica films on graphite

Hong Yang,<sup>a</sup> Neil Coombs,<sup>b</sup> Igor Sokolov<sup>a</sup> and Geoffrey A. Ozin\*<sup>a</sup>

<sup>a</sup>Materials Chemistry Research Group, Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

<sup>b</sup>Imagetek Analytical Imaging, 32 Manning Avenue, Toronto, Ontario, Canada M6J 2K4

It has recently been demonstrated that hexagonal mesoporous silica films can be grown at mica/water interfaces. In this report it is established that the films can also be synthesized on cleaved pyrolytic graphite. Diffraction and microscopy studies of the growth, structure and form of the films indicate that the channels are aligned along the hexagonal symmetry axes of the graphite surface. The registry of the mesoporous silica film with the underlying substrate may be facilitated by an organized hemicylindrical surfactant monolayer assembly that is observed at the boundary between the graphite and water. Growth of the mesoporous silica film most likely begins within a liquid-crystal surfactant/silicate film that is aligned with the hemimicelle–graphite overstructure.

The recently reported surfactant-based syntheses of hexagonal mesoporous silica films at air/water, oil/water and solid/water interfaces<sup>1-5</sup> raises a number of issues. These include the structure of the interfacial surfactant, details of the nucleation and growth processes, the factors that determine the alignment of the channels, and the domain and defect architecture of the films.

Here, we present experimental details relating to the growth, structure and form of a hexagonal mesoporous silica film deposited onto the surface of freshly cleaved pyrolytic graphite. A combination of powder X-ray diffraction (PXRD), high-resolution scanning electron microscopy (HRSEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM), provide converging evidence that the channels of the film appear to be aligned with the hexagonal symmetry axes of the graphite surface. A well ordered hemimicellar surfactant assembly is shown, by pre-contact electrical double layer (EDL) AFM, to pre-exist at the graphite/water interface. The polymerization of a pre-organised liquid-crystal surfactant/ silicate assembly located at the surface of graphite is believed to direct the nucleation and growth of the mesoporous silica film.

# Experimental

### Synthesis

The graphite used in this work is taken from a 12 mm  $\times$  12 mm  $\times$  2 mm pyrolytic graphite monochromator (Grade ZYB). This was a generous gift donated by the Advanced Ceramics Corporation. Thin sheets of graphite substrate were obtained by peeling a uniform section from the graphite block with Scotch tape and then cutting it into the desired size. Tetraethylorthosilicate (TEOS, 99 + %, Aldrich), cetyltrimethylammonium chloride (CTACl, 29 mass% aqueous solution, Pflatz & Bauer) and hydrochloric acid (36.5–38 mass% aqueous solution, BDH) were used as received. The synthesis of mesoporous silica films at the graphite/water interface was conducted under quiescent acidic conditions.<sup>1,2,6</sup> The reactant mole ratios used were 100H<sub>2</sub>O:7HCl:0.11 CTACl:0.1TEOS

The CTACl surfactant solution was mixed with the TEOS source of silica and stirred for *ca*. 2 min at room temperature and then transferred into a polypropylene bottle and allowed to achieve a stable air/water interface. A *ca*. 10 mm  $\times$  10 mm freshly cleaved pyrolytic graphite substrate was then positioned at the surface of the synthesis solution and allowed to float in

a horizontal position. The film forming process commenced within minutes under static conditions in an oven at 80 °C. Film growth was allowed to proceed for a period of one day to a week. The films so formed were transferred from the vessel using tweezers and washed with deionized water. The calcination of graphite-supported films was conducted in air and in a furnace attached to an Omega CN-2010 programmable temperature controller. The temperature ramp was <1°C min<sup>-1</sup> and typically the sample was held at 450 or 540°C for 4 h.

#### Characterization

**Powder X-ray diffraction.** PXRD data was obtained on a Siemens D 5000 diffractometer using Ni-filtered Cu-Ka radiation with l = 1.54178 Å. Samples of the graphite-supported films were mounted on top of a home-made low-background quartz cell for recording PXRD data.

Scanning electron microscopy. SEM images were obtained on a Hitachi S-4500 field emission microscope using a low acceleration voltage of 2-5 kV to minimize the charging of film surfaces. Samples were generally imaged directly except on one occasion when the sample was coated with a very thin layer of gold before imaging.

Transmission electron microscopy. TEM images of the films were recorded on a Philips 430 microscope operating at an



Fig. 1 A representative PXRD pattern for an as-synthesized mesoporous silica film grown on freshly cleaved pyrolytic graphite

accelerating voltage of 100 kV. In order to get ultrathin sections (100-300 Å) of the mesoporous silica film grown on graphite, a gold-coated film was embedded in epoxy, heated to form a block and cut at different angles using a diamond knife following the standard ultramicrotome procedure. The gold coating was used both to identify the film position in the epoxy block and the sides of the film, since the adhesion forces between the film and the graphite substrate are not sufficiently strong to withstand the microtome cutting force. Consequently the film is easily cleaved from the graphite upon sectioning.

Atomic force microscopy. AFM experiments were conducted on a NanoScope III microscope (Digital Instruments, CA) using silicon integrated tip cantilevers (Park Scientific Instruments, CA) for height mode scanning of the films, and special silicon cantilevers (Digital Instruments, CA, FESP type, 227 mm cantilever, resonance frequency 70-100 KHz) for tapping mode scanning in fluids. The cantilevers were used as received. Images of mesoporous silica film surfaces were obtained by using direct contact (dc) scanning mode. Images of CTACl assemblies on graphite were obtained by using two different methods. The first employed a pre-contact EDL height imaging mode. The second utilized a combined EDL pre-contact and tapping imaging mode. This method is a new way to image soft structures with minimal disturbance of their integrity. It was applied successfully in this work to image surfactant assemblies adsorbed at the graphite/water interface. CTACl aqueous solution with concentrations of 4-18 mM was used. The frequency of the cantilever tapping in the surfactant solution was about 33 KHz. To achieve pre-contact mode during tapping, the following procedure was adopted. After the tapping mode was engaged, the tip was elevated manually by the motor for the vertical displacements. Normally the elevation needed was about 100–200 nm. The jump into precontact mode was clearly evident every time.

### Results

The PXRD pattern of the film grown on graphite shows only two low-angle peaks assigned to the (100) and (200) reflections of a hexagonal symmetry mesoporous silica, Fig. 1. The absence of the (110) reflection for the film, compared to that of a randomly oriented powdered sample,<sup>7</sup> confirms that the channel axis is aligned parallel to the graphite surface. Calcination of the film was performed at 450 °C in air for 4 h. The high-temperature treatment causes the PXRD  $d_{100}$ -spacing to contract by 1–3 Å with concomitant changes in the intensity of the PXRD pattern. These effects are associated with the polymerization of residual SiOH groups. The integrity of the film and its mesostructure are well maintained throughout this thermal process.

SEM images of the films grown on the graphite substrate are shown in Fig. 2. The low-magnification images reveal that the films are essentially continuous, Fig. 2(*a*). Intriguing equilateral triangle-shaped pits are observed in the films, Fig. 2(*b*)–(*d*). Also, the growth fronts of the films typically have parallel filamentous extensions, terminated with edges inclined at 60° or 120°, and which sometimes display sharp 60° or 120° bends, Fig. 2(*a*), (*b*). The triangle-shaped pits display both straight and convex edges, Fig. 2(*b*)–(*d*). It is noteworthy that the edges of the triangles are exclusively aligned with respect to each other as well as in alignment with the edges of the



Fig. 2 SEM images of an as-synthesized mesoporous silica film grown on freshly cleaved pyrolytic graphite: (a) a large area and a growth front of the film; (b) a growth front showing the filaments and equilateral triangular pits (note that this sample has been coated with gold before imaging); (c), (d) close-up views of the triangular pits

filaments at the growing front of the film, Fig. 2(b). A closer examination of the inner walls of the triangular pits by HRSEM reveals a multi-layer topology with step features aligned with the sides of the triangles, Fig. 2(c), (d).

TEM images of the mesoporous silica films grown on graphite show that the channels are hexagonally close-packed with a centre-to-centre distance of about 40–45 Å and run parallel to the graphite/water growth boundary, Fig. 3(*a*). The TEM estimated unit-cell dimensions agree well with the PXRD  $d_{100}$ -spacings of 37–39 Å. A TEM image of a cross-section of the film cut along the channel axis is shown in Fig. 3(*b*). The observed parallel lines have a repeat distance of 40–45 Å which corresponds well with the separation of the walls of the mesopores and confirms that the channels grow parallel to the graphite surface. The smooth bottom surface of the films shown in Fig. 3 implies that it corresponds to the side of the mesoporous silica film that has grown from the graphite surface. The mesoporous silica films can be grown on graphite to a thickness of around 0.5–0.6 mm.

AFM is an effective probe of the topology of the films grown on graphite, Fig. 4. AFM direct contact (dc) mode images of the outer surface of the film reveal a mottled structure at the 50–200 nm length scale. A representative example of this texture on the surface of the film surrounding a triangular pit is shown in Fig. 4(*a*). Overall, these surface images portray the occurrence of a multi-layer step structure in the central regions of the films, Fig. 4(*b*), as well as on the walls of the triangular pits, Fig. 4(*a*). An on the filamentary growth fronts of the films, Fig. 4(*c*).

The organization of adsorbed surfactants at the boundary between water and silica, mica and graphite substrates has recently been observed using the pre-contact mode (EDL)



**Fig. 3** TEM images of an as-synthesized mesoporous silica film showing (*a*) the hexagonally closed-packed channel structure with a centre-to-centre spacing of *ca.* 45 Å; (*b*) the channels running parallel to the graphite surface. Bottom (smooth side), grown at the graphite/water interface; top (rough side), grown in solution. (Note, imaging the entire film compromises visualization of the channels.)

AFM soft imaging technique.<sup>5,8–10</sup> We have found in this study that the perturbation of the surfactant assembly by the scanning tip can be further reduced and the quality of the AFM images enhanced by using the tapping mode in conjunction with the pre-contact (EDL) technique.

This can be understood by recalling that the EDL consists of a bilayer of oppositely charged surfactant cations and counter anions adsorbed on the AFM tip. The result is an additional EDL force of repulsion between the tip and the surfactant assembly, adsorbed on graphite, being imaged. Thus, the apex of the tip floats over the fragile surfactant assembly with a gentler type of interaction. This type of pre-contact scanning mode, in conjunction with the tapping action of the probe, will cause less deformation of the assembly being imaged because of a lack of friction force.

According to previous experiments, and our own work, the direct pre-contact mode scanning along the boundary of the EDL provides an image of the adsorbed hemicylindrical surfactant monolayer assembly on the graphite surface. The evidence for this being a hemimicellar monolayer comes from the thickness measurement of the surfactant assembly. This is achieved by increasing the scanning force, whereby the EDL repulsion is overcome and the tip jumps through the film.<sup>5,8–10</sup>

Pre-contact (EDL) tapping mode AFM images of an aqueous solution of CTACl adsorbed on graphite have been obtained over the concentration range of 4-18 mm. One can discern well defined parallel stripes with a periodicity of ca. 53 Å, Fig. 5(a), and a thickness up to 500 Å, Fig. 5(b). The film thickness was estimated by measuring the height difference when the tip jumps from the pre-contact tapping to the contact tapping mode. The collapse of the surfactant assembly was either spontaneous or induced by the change in the setpoint of the AFM scanning. This implies the existence of up to 10 layers of 50 Å diameter surfactant cylindrical micelles organized as a liquid-crystal film at the boundary between water and graphite. The AFM images also reveal the presence of domains within which parallel arrays of cylindrical micelles meet at boundaries with either  $60^{\circ}$  or  $120^{\circ}$  angles, Fig. 5(c). This suggests that the director of the liquid-crystal overlayer is aligned with the hexagonal unit-cell axes of the graphite surface as well as the axis of the adsorbed hemicylindrical micellar monolayer. The ability to observe, for the first time, such surfactant multilaver assemblies without their destruction apparently stems from the lack of friction force in the AFM tapping mode compared to that of the direct contact mode.

### Discussion

The above results provide a basis for beginning to understand the origin of the preferred orientation and apparent registry of the channels of the mesoporous silica film with the hexagonal symmetry axes of the graphite surface.

The assembly process in the absence of TEOS probably begins with adsorption of CTACl on the graphite surface. The hydrophobic interaction between the alkane chain and the graphite causes the surfactants to lie flat on the surface.8,9 Geometrical matching of the methylene groups in the all-trans alkane chain with the aromatic carbon six-rings in the planar graphite surface, favours a head-to-head and tail-to-tail packing arrangement of the surfactant along the hexagonal symmetry axes of graphite. This geometry is driven by hydrophobic, electrostatic ion-pair and image dipole forces between the CTACl and the electrically conducting graphite surface.<sup>8,9</sup> The result is 50 Å parallel stripes of surfactants running orthogonally to the graphite hexagonal symmetry axes. This organized surfactant monolayer assembly then serves as a template for the further adsorption of CTACl from solution and the formation of a monolayer of 50 Å diameter hemicylindrical micelles with a thickness of ca. 25 Å.<sup>8,9</sup> Using pre-contact AFM imaging mode we have reproduced this



Fig. 4 AFM dc mode images of the outer surface of an as-synthesized mesoporous silica film on graphite: (a) mottled texture on the film surrounding a triangular pit; (b) steps on the edges of the triangular pits; (c) terraces on the filaments at a growth front

result over the 4–18 mM surfactant concentration range investigated in this study. However, for a surfactant concentration above roughly 9 mM and when the AFM imaging is changed to the pre-contact tapping mode, we still observe 50 Å parallel stripes but now with a film thickness of about 500 Å, Fig. 5(*b*). This implies that continued accretion of CTACl from solution leads to the development of a multilayer of close-packed 50 Å diameter cylindrical micelles. These are presumably organized in the form of a liquid-crystal film registered with the graphite surface.

In the presence of TEOS, nucleation of the mesoporous silica film is initiated by polymerization of charge-balancing silicate anions in the headgroup region of a liquid-crystal film that has its director axis registered with the hexagonal symmetry axes of the underlying graphite substrate, Plate 1. Growth of the mesoporous silica film is likely to be determined by the charge and structure encoded in the surfactant/silicate/ graphite film. This process could produce a mesoporous silica film in which the channels are aligned with the hexagonal symmetry axes of the graphite surface. Subsequent deposition and polymerization of surfactant/silicate micellar assemblies results in the continuous growth and thickening of the mesoporous silica film up to the observed value of about half a micrometre.

This templating model for the polymerization of a surfactant/ silicate liquid-crystal film on graphite is consistent with the observation of mutually aligned triangular-shaped pits in the body of the resulting mesoporous silica film, which are themselves in alignment with the edges of the filaments that comprise the growth fronts of the film. These structural features likely arise from the ability of the surfactant/silicate/graphite assembly to control the alignment of the channels in the growth of the mesoporous silica film, along the three symmetry equivalent hexagonal axes of graphite. Growth fronts are expected to meet at  $60^{\circ}$  in the body of the mesoporous silica film to form triangular features and to terminate at the extremities of the film to create filaments displaying  $60^{\circ}$  and  $120^{\circ}$  angular features, Fig. 2.

The stepped textures observed for the films, the triangular pits and the filaments, Fig. 4, most likely originate from polymerization and growth of cylindrical surfactant/silicate seeds<sup>11</sup> in the liquid-crystal film adsorbed on the graphite surface. Further studies will be required to elucidate the details of the nucleation and growth processes that give rise to these mesoporous silica films.

## Conclusion

In this paper, we have demonstrated that mesoporous silica films can be synthesized on the hydrophobic surface of freshly cleaved pyrolitic graphite. Our combined PXRD, HRSEM, TEM and AFM data provide converging evidence that the channels of the film are probably registered with the hexagonal symmetry surface structure of the underlying graphite. This arrangement can be understood in terms of the growth of the mesoporous silica film within a liquid-crystal surfactant/silicate



**Fig. 5** Pre-contact (EDL) tapping mode AFM images (using phase detection) of CTACl assemblies adsorbed on graphite showing (*a*) parallel stripes with a periodicity of *ca.* 53 Å, and (*b*) a thickness of *ca.* 500 Å; (*c*) domains of surfactants with parallel arrays of cylindrical micelles that meet at sharp boundaries with an angle of either 60° or 120°. The surfactant concentration was in the range of 9–18 mM.



**Plate 1** Graphical illustration of proposed model for the formation of a mesoporous silica film on graphite. Red, surfactant tail; yellow, surfactant headgroup; light blue, silicate building-block; dark blue, silica; black, graphite.

film that is aligned with the symmetry axes of graphite. Overall, the synthesis of mesoporous silica films on hydrophilic mica and hydrophobic graphite surfaces, as well as free-standing ones formed at the boundary between air and water, augurs well for their use in a range of applications, such as large-molecule catalysis, membrane separations and chemical sensing.

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