# ETCHING OF COMPLEX NANOPORES IN CRYSTALLOGRAPHIC DIRECTIONS BY COBALT-CATALYZED CARBON HYDROGENATION

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Introduction

Solid-state nanometer-sized pores (nanopores) are widely used for the rapid electrical detection and characterization of single biopolymer molecules such as DNA and RNA [1-3]. Existing simple nanopore synthesis methods mostly require transmission electron microscope (TEM) beams or focused ion beams (FIB) [4,5]. However, for many practical applications, it is desirable to develop a relatively simple and efficient method to manufacture nanopores, especially complex nanopores. Here we focus on creating complex nanopores by the action of cobalt nanoparticles in high-temperature environments containing hydrogen. It has long been known that the reaction between carbon and hydrogen is strongly catalyzed by metals such as iron, cobalt and nickel [6-8]. Catalytic nanoparticles are usually active on edge-plane surfaces, and often follow well-defined crystallographic directions. Ordered carbon films almost always consist of graphene layers arranged parallel to the substrate, making the synthesis of nanopore membranes difficult as it requires particle etching in a basal attack mode to produce pores that connect the front and back sides of the membrane. Here we propose a novel solution that uses chromonic liquid crystal precursors to make carbon thin films, in which the graphene layers lie perpendicular to the plane of the film, and potentially allow the synthsis of. individual permeating nanopores in the natural crystallographic etching mode. The synthesis conditions, crystallographic etching rules, and applications for such controlled nanopore membranes will be discussed in this paper.
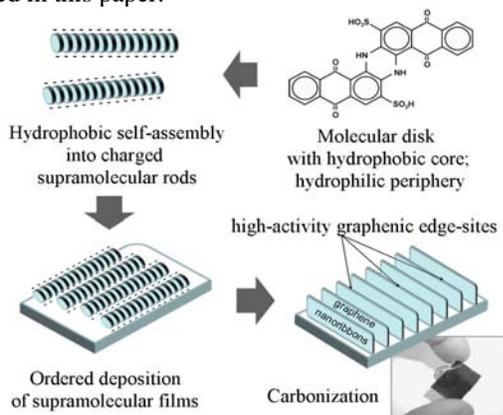

Fig. 1. Schematic of the synthesis method for carbon thin films from chromonic liquid crystal precursors. The film is oriented with all graphene layers lie perpendicular to the substrate [9].

Experimental

Indanthrone disulfonate and related water-soluble polyaromatic dyes were used as the precursors to make films on quartz plates by using Meyer-bar (RD Specialties Inc., Webster, NY) coating method. The hydrophobic faces of these molecules (Fig. 1) combined with their hydrophilic peripheral regions cause the formation of massive π-stacks in the aqueous phases leading to supramolecular rods that exhibit lyotropic liquid crystalline ordering above a threshold concentration. During Mayer-bar application, the shear flow in the gaps at the interface of the substrate and bar aligns the rod-like aggregates parallel to the bar rubbing direction, which in turn aligns the disk-like building blocks with their molecular planes perpendicular to both the substrate and rubbing direction. These "chromonic" liquid crystal films were then dried and carbonized by directly heating in nitrogen at 700 °C for 30 min. During the carbonization process, the polymerization reactions lead the neighboring molecular disks to crosslinke and merge into continuous graphene layers. This synthesis step converts the organic thin films into novel carbon films which are oriented over the entire substrate surface. As shown in Fig. 2, the carbon films "capture" the supramolecular structure of organic films in this thermal carbonization step which was examined by polarizing filters. The thickness of these carbon films depends on the concentration of chromonic liquid crystal solutions and the bar sizes. The carbon films in this paper were approximately 150 nm in thickness measured by FIB.

Cobalt nanoparticles <50 nm (from Strem Chemicals, MA) were diluted to approximately 10 ppm in ethanol solution. After 15 min of bath sonication, the precursor solution was immediately deposited onto the carbon films. Catalyst loaded samples were then placed in a fused silica tube furnace, and heated at 700 °C for 30 min and 900 °C for 2 h under a high purity gas flow containing $H_2(1\%)$ and $He(99\%)$. The samples were cooled down to room temperature in the same gas environment and then examined in detail by Scanning Electron Microscopy (SEM).
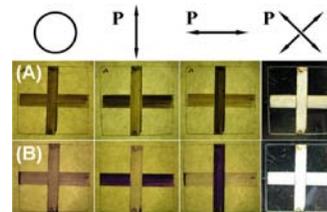

Fig. 2. Digital photographs of optically anisotropic thin films on quartz (25×25mm) under different polarization conditions. (A) Carbon thin films; (B) Original organic thin films. Carbonization conditions were 700 °C for 30 min in nitrogen.

Results and Discussion

We first established that gasification etching does not occur on the surface of these carbon films at temperatures below 600°C.

Upon heating at 700 °C for 30 min, however, some cobalt particles have started to etch on the top surface of the carbon

film (Fig. 3(C)). Cobalt particles are observed to adhere to the walls of the pores created. The pore sizes were uniformly similar to but slightly larger than particles themselves. It is well known that the catalytic gasification of carbon occurs by the dissociation of molecular hydrogen on metal particles [8] and contact is necessary for the catalytic reaction. As anticipated, the dominant etch direction in Fig. 3 is perpendicular to the substrate plane (thus parallel to the graphene layer planes implying edge attack).
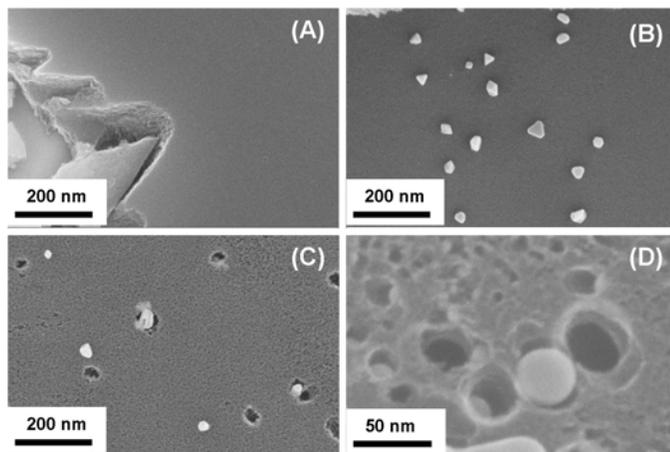
Fig. 3. SEM images demonstrating the gasification etching reaction in various steps. (A) The carbon thin film before doping or reaction. The surface is flat and smooth with a thickness around 150 nm; (B) Cobalt nanoparticles (<50 nm) loaded on the surface prior to reaction; (C) A sample heated at 700 °C for 30 min under a gas flow of $H_2(1\%)$ + $He(99\%)$; (D) A sample heated at 900 °C for 2 h under a gas flow of $H_2(1\%)$ + $He(99\%)$.
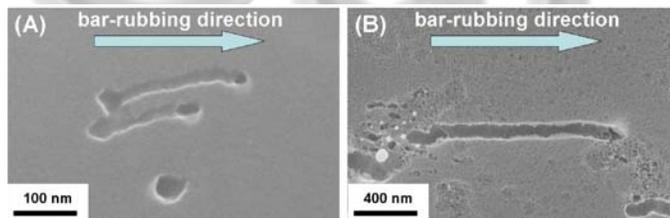
Fig. 4. SEM images of a sample heated at 900 °C for 2 h under a gas flow of $H_2(1\%)$ + $He(99\%)$. (A) The bottom side (B) The top side.

Cobalt nanoparticles on carbon films were also investigated at slightly higher temperature 900°C for 2 h. As shown in Fig. 3(D), most cobalt nanoparticles had already etched down through the carbon film and some particles had penetrated the film transversely by following graphene layer edge surfaces which are more reactive than the graphene layer faces. It is worth to note that the cobalt nanoparticles morphology changed during the process, some became spherical and some of them tended to stick together in this high-temperature environment suggesting some fusion. However, most nanoparticles did not have the chance to aggregate due to the very dilute precursor solution.

To confirm that some of the cobalt nanoparticles have penetrated the film, the sample was removed from quartz using double-sided black electrical tape, and then the bottom side of the carbon film was examined by SEM. Fig. 4(A) clearly shows the pores at the bottom side created by cobalt nanoparticles. It is interesting that some particles did not stop etching after they reached the bottom of the carbon film, but formed channels parallel to the substrate plane. These would be complex channels with vertical and horizontal segments driven by both crystallographic plane selection and by the confining effect of the substrate. Surprisingly, we found that the below-surface horizontal channel segments were not parallel to the graphene planes, but rather perpendicular to them and parallel instead to the preferred bar rubbing direction. One possible explanation for this unexpected directional selection is the effect of adhesive energy. Since the graphene layer edges are more reactive, the gasification reaction occurs more easily in those graphene layer edges which are in the immediate vicinity of the catalyst particles. After a period of reaction, the cobalt particles may lose contact with the edges. In contrast, the graphene layer planes lying at 90 and 270 degrees still maintain contact with the particles. Due to the existence of defects in the graphene layers, the gasification reaction was slower but continuous along the bar-rubbing direction in response to the adhesive force which maintaining the contact with the graphene layer faces. More work is needed to understand channel shape and direction selection in these unique materials.

Conclusions

We have presented a new technique of synthesis individual nanopores on novel carbon films. A possible reaction mechanism explaining the formation of nanopores and nanochannels was described in this paper. The created pore sizes can achieve 20 nm in diameter which mainly depends on nanoparticles sized used in the synthesis process.

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