

SURFACE MORPHOLOGY OF CARBON AEROGELS BEFORE AND AFTER HEAT TREATMENT

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1. Introduction

Carbon aerogels are a family of low-density microcellular materials characterized by low mass densities, ρ_m , relatively large specific surface areas (600-800 m²/g), and very high porosities. These materials demonstrate intriguing structure-property relationships along with the potential for being used as adsorbents, thermal insulators, and electronic devices, such as double layer capacitors and devices for water purification.¹⁻⁵

Depending on the details of their synthesis, carbon aerogels exhibit two morphological types, polymeric and colloidal, each with its distinct structural characteristics. The aerogels of both types are built up by kinetic aggregation of molecular clusters, which can be characterized by studying their pore structures. The smallest, "primary particles," contain nanopores (< 20 Å) and cluster together into a network of "secondary particles," which give rise to mesopores (20-500 Å). The secondary particles are, in turn, strung out in chains to create the porous matrix of the aerogel, with macropores (> 500 Å) located between chains.

In the last few years, we used a variety of techniques to investigate the structure-property relationships inherent in this important family of materials. Raman spectroscopy,^{6,7} transport⁶ and photoconductivity^{8,9} measurements, and high resolution transmission electron microscopy (HRTEM)¹⁰ have all been used to ascertain the structure and morphology of carbon aerogels.

In the present work, we have characterized, for the first time, the effects of heat treatment on the surface morphology and pore structure of different types of carbon aerogels by a direct surface measurement technique, atomic force microscopy (AFM).

2. Experimental

The carbon aerogel samples used for this study were derived from the pyrolysis of resorcinol-formaldehyde (RF) aerogels.¹¹ Carbon aerogels were obtained from the RF aerogels via pyrolysis in a 3-zone Lindberg furnace under nitrogen flow. The furnace was ramped

to 1050° C in approximately 16 hours and held at this temperature for 4 hours. For this work, we also studied a series of heat-treated samples ($T_{HT}=1500-1800^{\circ}\text{C}$ for 4 hours) to ascertain the effects of heat treatment on the pore structure of aerogels.

To image the aerogel samples, we prepared special AFM microtips with very high aspect ratios to allow imaging of highly porous aerogel surfaces. The deposition of these microtips was done in the scanning electron microscope (SEM) by exposing a single spot on the prefabricated silicon AFM tip (which was additionally coated with 20 nm Au) to the electron beam for a few minutes in the presence of hydrocarbon contamination in the SEM chamber. Decomposition of these "contamination" gas molecules by high-energy primary and secondary electrons from the incident beam results in the deposition of thin (~100 nm in diameter at the base of the tip), tall (up to 5 μm) carbon filaments on top of the prefabricated AFM tip. The end radius of curvature and opening angle of the terminal cone of the AFM tip were consistently about 20 nm and 5-10°, respectively.

We have used such AFM tips enhanced via the electron beam deposition (EBD) technique to perform a series of systematic AFM studies of carbon aerogel materials as a function of the heat treatment temperature.

3. Results and Discussion

Figure 1 shows typical 800nm \times 800nm scans of a high-density polymeric aerogel as-prepared (a), and heat-treated at $T_{HT} = 1800^{\circ}\text{C}$ (b). The heat-treated aerogel looks distinctly different from as-prepared samples, with its particles "fused" together into large clusters, with a lot of space between these clusters. It appears that heat treatment at this high temperature causes an aggregation of primary and secondary aerogel particles into large graphitized agglomerates, possibly causing the partial collapse of the aerogel network. It should be noted that treatment at 1500°C appears to have no such effect.

This same process of particle aggregation as a result of heat treatment can also be seen on a larger scale (50 $\mu\text{m}\times$ 50 μm) in going from Fig. 2(a) (high-density

polymeric aerogel, as-prepared) to Fig. 2(b) (same aerogel, after heat treatment at 1800°C). Clearly, the porous structure (on this scale) of as-prepared aerogels is largely lost (flattened out) as a result of heat treatment.

These observations are consistent with our earlier Raman spectroscopy⁷ photoconductivity,⁹ and magnetic susceptibility⁹ studies, where it was found that heat treatment anneals the microscopic disorder in aerogels to a large degree (although not completely), inducing in-plane order development (a low degree of graphitization). Generally, the onset of a low degree of graphitization at heat treatment temperatures in the range 1500°C < T_{HT} < 1900°C has been shown to be typical for a wide variety of hard carbon materials, such as certain carbon fibers and carbon blacks.^{12,13}

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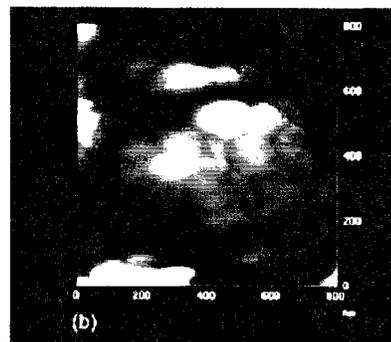
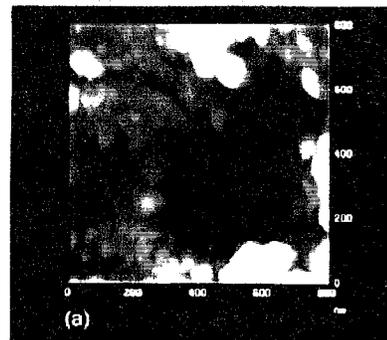


FIG. 1. Typical 800nm×800nm AFM scans of a high-density polymeric aerogel as-prepared (a), and heat-treated at $T_{HT} = 1800^\circ\text{C}$ for 4 hours (b).

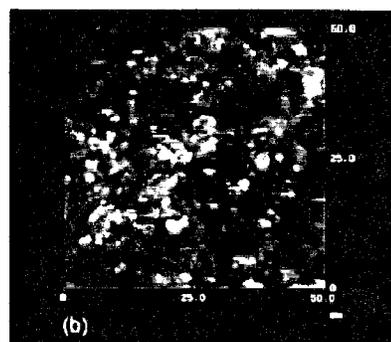
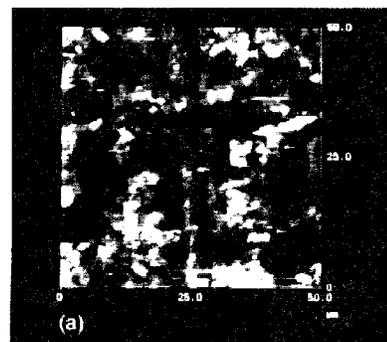


FIG. 2. Typical large-scale (50 μm ×50 μm) AFM scans of a high-density polymeric aerogel as-prepared (a), and heat-treated at $T_{HT} = 1800^\circ\text{C}$ for 4 hours (b).