

## Negatively curved spongy carbon

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We describe the production and characterization of a form of nanostructured carbon consisting of fully connected, three-dimensional (3D)  $sp^2$  networks. This form of carbon is characterized by interconnected thin layers forming a spongy structure with meso- and macroporosity. It is produced by a pulsed microplasma cluster source in the presence of a very low concentration of metallorganic catalyst. The unique 3D structure and topology of the spongy carbon are very interesting for catalysis and electrochemical applications and for the investigation of negatively curved forms of carbon such as schwarzites. © 2002 American Institute of Physics. [DOI: 10.1063/1.1516635]

Nanostructured carbon-based solids represent a class of materials where the surface curvature and the organization of structures in a range from the fraction of a nanometer to a few hundreds of nanometers dramatically influence the mechanical, chemical, and physical properties.<sup>1</sup> Porous carbon networks are of great importance in many areas of science and technology, including catalysis, energy storage, chromatography, gas and liquid purification, and molecular sieving.<sup>2,3</sup> The high specific surface area, chemical inertness, and large pore volumes are the important parameters for these applications.

The pores are classified as macropores (diameter >50 nm), mesopores (2 nm <diameter<50 nm) or micropores (0.8 nm<diameter<2 nm). In conventional activated carbons, most pores are micropores and this is detrimental for many applications requiring meso- and macropores for the penetration of macromolecules and ions.<sup>2</sup> The complexity of the carbon structure makes the control of the pore size and structure a difficult technological problem which is not yet solved.<sup>2,3</sup>

Many synthetic routes have been proposed for the production of meso- and macroporous carbons based on catalytic activation,<sup>3</sup> the assembly of submicron carbon fibers<sup>2</sup> and the carbonization of templates.<sup>4,5</sup> The latter method produces ordered structures for catalytic and photonic applications.<sup>4,5</sup>

The creation of nanoparticles with a specific surface curvature can also be used to control the porosity. For example, materials based on nanotubes or related carbon nanostructures show micro- and mesoporosity attractive for electrochemical applications.<sup>6,7</sup> Structures with the negative curvature analog of fullerenes have been proposed as porous carbons with interesting structural and functional properties.<sup>8,9</sup> The Gaussian curvature of a closed surface area  $S$  with graphitic tiling can be defined in terms of the number

of pentagonal ( $p$ ) and heptagonal rings ( $t$ ) in this surface as  $K = (p - t)\pi / (3S)$ , where  $K$  is the average Gaussian curvature of the surface. Hence, an excess of pentagons creates a positive curvature as in the fullerenes, while an excess of heptagons or higher-order rings creates a negative curvature, as here.<sup>1,8,9</sup> The existence of such three-dimensional, negatively curved ordered or amorphous  $sp^2$  coordinated carbon networks has been proposed in the form of infinite, triply periodic minimal surfaces called schwarzites.<sup>8</sup>

Total energy calculations have shown that carbon schwarzites are more stable than fullerenes of similar absolute Gaussian curvature.<sup>8,9</sup> This suggests that negatively curved carbon networks may be formed during the carbon-arc synthesis of fullerenes and nanotubes. However, such networks have not been observed so far in fullerene or nanotube soot.

In this letter, we report the production and characterization of a form of nanostructured carbon consisting of three-dimensional, fully connected  $sp^2$  negatively curved networks. The nanostructured carbon is characterized as a low-density, spongy structure based on pores with diameters ranging from 50 to 600 nm. We show that it can be produced in macroscopic quantities and deposited as a film using supersonic cluster beam deposition. The formation process occurs in the presence of traces of metallorganic species. The porosity of the structure can be controlled by using different metallorganic precursors.

Spongy carbon networks have been produced and deposited by a pulsed microplasma cluster source (PMCS).<sup>10</sup> A detailed description of the PMCS and of the deposition method have been published elsewhere.<sup>10,11</sup> Briefly, the PMCS consists of a ceramic body with a channel drilled to intersect perpendicularly to a larger cylindrical cavity. The channel hosts the two carbon electrodes. A solenoid valve faces one side of the cavity. The other side of the cavity is closed by a nozzle for the formation of a supersonic beam.<sup>11</sup> A helium pulse, delivered by a solenoid valve, is directed against the graphite cathode and it is ionized by a pulsed

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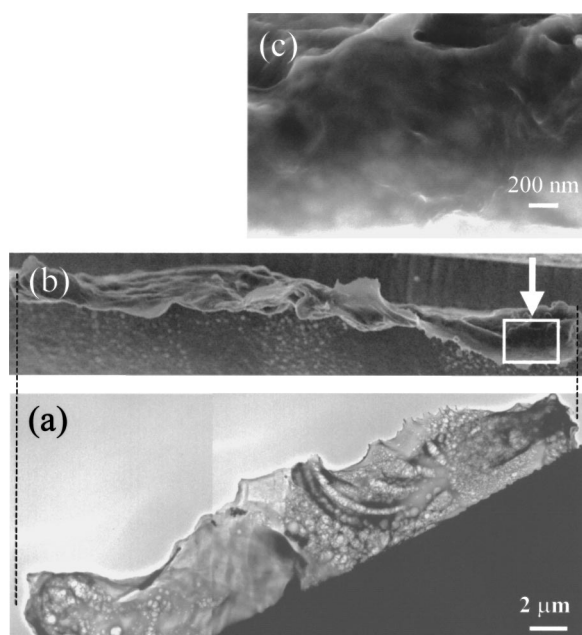


FIG. 1. (a) TEM micrograph of the spongy carbon film produced with Mo, showing the uniformly distributed porous structure. (b) The same region in a scanning electron microscopy (SEM) micrograph showing the complex three-dimensional structure. The overall thickness, varies between 70 nm in the central part and 2  $\mu\text{m}$  at the extremes. (c) High-resolution SEM image of the region in the white frame in (b). The voids present in the bulk of the material causes the bubblelike regions with different contrast.

voltage of 500–1500 V. The helium plasma ablates the cathode surface, removing carbon atoms via sputtering. During standard operation, the mean He pressure in the source cavity is roughly 30 Torr.

In the PMCS, the vaporization of carbon and the formation of nanoparticles occurs in a different way than in a typical fullerene or nanotube arc discharge.<sup>10</sup> The ablated carbon condenses in a high-pressure region in front of the cathode, forming carbon clusters with a structure and a mass distribution that has been extensively described in Ref. 12.

Metal catalysts can be added during the cluster forma-

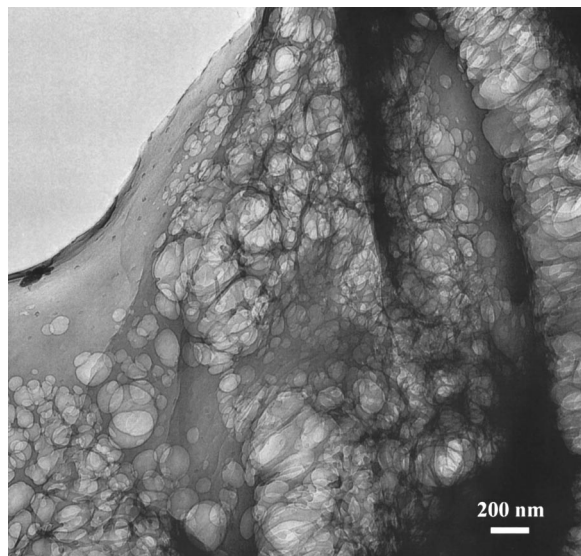


FIG. 2. TEM micrograph showing a spongy carbon region at high magnification. The contrast variations arise from variations of the film thickness in the direction parallel to the electron beam.

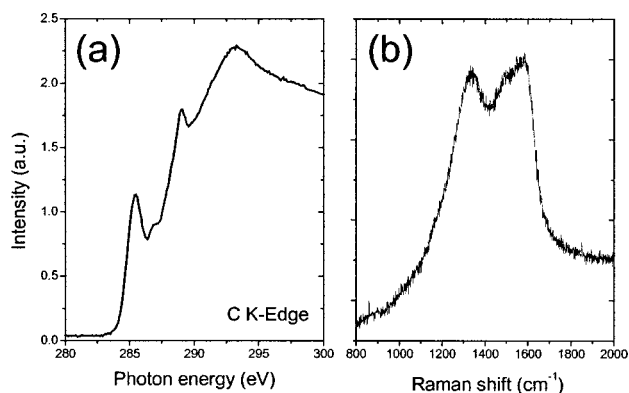


FIG. 3. (a) NEXAFS spectrum of the sample at carbon *K* edge indicating  $sp^2$  hybridized carbon. No signature from molybdenum has been observed due to the high dilution of metal into the material. NEXAFS characterization was performed at LURE (France), on the vacuum ultraviolet Super-ACO storage ring, using the SACEMOR beam line. (b) Raman spectrum typical of a highly disordered graphitic character. Raman spectra have been obtained with a Renishaw MicroRaman System 2000 with spatial resolution of roughly 1  $\mu\text{m}$ . A He–Ne laser ( $\lambda=635$  nm) has been used. No modification of the samples has been observed under prolonged irradiation.

tion by using mixed carbon–metal cathodes.<sup>13</sup> With a mixed graphite–metal (Mo or Co) electrode, we were able to deposit nanostructured films rich in multiwalled nanotubes, closed polyhedral particles, carbon socks and large metal and carbide clusters.<sup>14</sup>

Metallic precursors can be also added by bubbling the He gas stream through a liquid metallorganic compound prior to injection into the PMCS. The metallorganic molecules in the buffer gas are cracked by the electric discharge, thus providing metal atoms and highly reactive radicals to the condensing carbon vapor. The amount of the metallorganic species injected can be controlled by the bubbler temperature. For these experiments, we have used Molybdenum (V) isopropoxide  $\text{Mo}(\text{OC}_3\text{H}_7)_5$  in isopropanol and Cobalt (II) methoxyethoxide  $\text{Co}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  in 2-methoxyethanol. The operating conditions of the PMCS were the same as used for standard carbon cluster production.<sup>11,14</sup>

Figure 1(a) shows a transmission electron microscopy (TEM) image of the morphology obtained using molybdenum as precursor. Figure 1(b) shows the same region as Fig. 1(a) as a projection image: The material looks like a self-standing film made by several interconnected undulated foils. In high-resolution scanning electron micrograph [Fig. 1(c)], the contrast created by secondary electrons shows that voids are present in the bulk of the sample indicating that the material has a complex three-dimensional porous structure.

Figure 2 shows a higher magnification TEM image of the same region. The contrast variations arise from variations of the film thickness in the direction parallel to the electron beam. Maximum contrast corresponds to regions where the electron beam is highly scattered from the spongy material, i.e., where the number of overlapping layers is large. In regions where deep interconnected cavities can be seen, features at different heights about the eucentric plane have different—and not exact—focus conditions (dark to bright Fresnel fringes from over to under focus). Tilting experiments at low angles (below  $20^\circ$ ) have been performed showing that the regions of maximum contrast are shifted as the

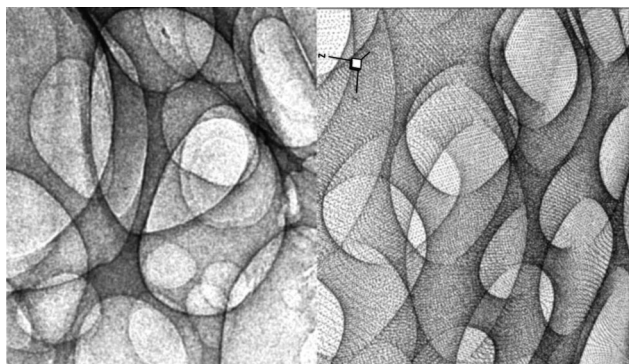


FIG. 4. A small portion of the TEM image shown in Fig. 1 (Left) compared to a projection of the surface generated by Eq. (1) onto a plane normal to the  $z$  direction for  $\beta=0.7$  and  $10-3\pi < z < 10+5\pi$  (Right).

beam crosses the sample at different angles. These observations confirm the three-dimensional nature of the material. The structure of the spongy carbon consists of thin carbon layers (1–2 nm thickness) interconnected to form a network with overall thickness up to 2  $\mu\text{m}$ . The formation of the spongy carbon is assisted by the presence of a metal catalyst: The catalyst concentration and dispersion seem to determine the final curvature and morphology of the material.

Comparing the material obtained with mixed cathodes with that obtained with metallorganics, we have verified that the presence of large catalyst concentrations (several percent) in the form of relatively large clusters favors the production of carbon nanoparticles, whereas a finely dispersed catalyst at a low concentration drives the growth to the formation of spongy networks. Generally, the physical vapor deposition of carbon nanostructures uses mixed cathodes, which gives a high local concentration of catalyst particles.<sup>12,14</sup> By changing the metallic precursors, it is also possible to control the porosity of the material. For example, cobalt leads to networks of narrower pores than those formed with Mo.

The spongy carbon consists of a fully  $sp^2$  three-dimensional structure, as confirmed by Raman and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy (Fig. 3), in contrast to fullerenes, nanotubes, and graphite, which are zero-, one-, or two-dimensional covalent structures linked together by van der Waals forces. TEM images suggest a topological structure similar to that of sponge minimal surfaces.<sup>15</sup> Such carbon sponges should have the topological structure of random schwarzites.<sup>8</sup>

A reconstruction of the actual three-dimensional structure is not possible from TEM images, however a useful comparison can be made with simulated images originating from the projection of a model analytical surface with suitable topological requisites. In order to simulate extended regions of the observed interconnected layers as they appear in TEM images, we use a model analytical surface defined by

$$\cos(xz^{-\beta}) + \cos(yz^{-\beta}) + \cos\left(\frac{z^{1-\beta}}{1-\beta}\right) = 0, \quad (1)$$

where the coordinates  $x$ ,  $y$ , and  $z$ , are expressed in a conventional unit, here  $2\pi$  times the unit cell size of the smallest  $p$ -type schwarzite  $a=7.77$  Å.<sup>8,16</sup> This analytic form describes a schwarzite<sup>17,18</sup> which has been distorted along a

given axis  $z$ , assumed as the growth direction, by a scaling factor  $z^\beta$ . For  $\beta=0$ , this form approximates very well a minimal three-periodic  $p$ -type schwarzite. In Fig. 4, we show a comparison of a portion of a TEM image and a plot of a projection of Eq. (1) along the  $z$  axis for  $\beta=0.7$  and  $10-3\pi < z < 10+5\pi$ . The similarity between experiment and simulation is striking. A similarly good qualitative correspondence between the experimental and simulated TEM images is found for other parts of the sample. This agreement, with the observed pure  $sp^2$  bonding, suggest that our films indeed have a structure based on negatively curved interconnected layers similar to a random schwarzite.

In conclusion, we have reported the formation of negative-curvature highly connected  $sp^2$  carbon networks. The possibility of depositing films containing this form of spongy carbon allows the production of nanostructured carbon not only with controlled porosity on the nano-, meso-, and macroscale, but also with controlled topology and physicochemical properties. The extremely high porosity and low density of the material suggest many possible applications especially for catalysis, gas and energy storage, and templating of biomaterials. These carbon sponges should also be good candidates for the investigation of negatively curved carbon networks and, in particular, of the long-sought topological structure of random schwarzites.<sup>19</sup>

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