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SYNTHESIS, CHARACTERIZATION, AND MODELING OF HYDROGEN STORAGE IN CARBON AEROGELS

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Abstract

Carbon aerogels are a special class of open-cell foams with an ultrafine cell/pore size (<50 nm), high surface area (600-800 m^2/g), and a solid matrix composed of interconnected colloidal-like particles or fibers with characteristic diameters of 10 nm. These materials are usually synthesized from the sol-gel polymerization of resorcinol-formaldehyde or phenolic-furfural, followed by supercritical extraction of the solvent and pyrolysis in an inert atmosphere. The resultant aerogel has a nanocrystalline structure with micropores (<2 nm diameter) located within the solid matrix. Carbon aerogel monoliths can be prepared at densities ranging from 0.05-1.0 g/cm^3, leading to volumetric surface areas (> 500 m^2/cm^3) that are much larger than commercially available materials. This research program is directed at optimization of the aerogel structure for maximum hydrogen adsorption over a wide range of temperatures and pressures. Computer modeling of hydrogen adsorption at carbon surfaces was also examined.

Introduction

Aerogels have a unique morphology in that *both* the covalently-bonded particles of the solid phase and the interconnected pores of the gas phase have nanometer-sized dimensions. This structure leads to extremely high surface areas (400-1100 m^2/g) with a large fraction of the atoms covering the surface of the interconnected particles. Sol-gel polymerization conditions can be used to engineer the particle size, particle interconnectivity, and pore size in these materials.

The polycondensation of (1) melamine with formaldehyde, (2) resorcinol with formaldehyde, and (3) phenolic with furfural are three proven synthetic routes for the formation of organic aerogels. The latter two materials can also be pyrolyzed in an inert atmosphere to give carbon aerogels. Carbon aerogels are the first electrically conductive aerogels to be synthesized, and they are finding applications as electrodes in energy storage devices. In this paper, we discuss the chemistry-structure-property relationships of carbon aerogels as they relate to hydrogen adsorption under cryogenic conditions.

Technical Approach

Synthesis

The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [Pekala 1992]. Briefly, resorcinol (1,3 dihydroxybenzene) and formaldehyde were mixed in a 1:2 molar ratio, respectively. Deionized/distilled water was added as the diluent and sodium carbonate as the base catalyst. After stirring to form a homogeneous solution, the mixture was poured into glass vials, sealed, and cured at elevated temperature (50-85 °C). Upon completion of the cure cycle, the crosslinked gels were exchanged with acetone and subsequently dried from supercritical carbon dioxide ($T_c = 31°C$; $P_c = 7.4$ MPa). This procedure resulted in the formation of monolithic RF aerogels in cylindrical form (25 mm diameter x 60-85 mm long). The monoliths were then pyrolyzed (600-1100 °C) in flowing nitrogen to form carbon aerogels.

Phenolic-furfural (PF) gels were prepared from a commercially available polymer solution (FurCarb UP520; QO Chemicals, Inc., West Lafayette, IN) [Pekala, in press]. This solution was composed of approximately a 50:50 mixture of a phenolic novolak resin dissolved in furfural. The Furcarb UP520 was diluted with 1-propanol and 10 phr catalyst (a mixture of aromatic acid chlorides; Q2001; QO Chemicals, Inc., West Lafayette, IN) was added. Solutions prepared with different amounts of diluent were then poured into glass vials, sealed, and cured for 7 days at 85 °C. A small amount of syneresis was observed during the cure cycle, allowing the gels to be easily removed. PF gels were supercritcally dried and pyrolyzed in the same manner as RF gels.

Adsorption Measurements

Hydrogen adsorption measurements were performed in an apparatus similar to that shown in Figure l. Carbon aerogels were heated at ~250 °C and resorcinol-formaldehyde aerogels at ~150 °C under vacuum in sample holder "A" to remove surface contaminants (e.g., water). The sample holder was then submerged in liquid nitrogen (77 K), and hydrogen (99.999 %) was bled slowly through a set of control valves from reservoir "B" into "A". The pressure in "A" was monitored as a function of the hydrogen delivered. The total volume of the carbon aerogel was calculated from the skeletal density measured by helium pycnometry. Next, a stainless steel "plug" of the proper volume was inserted into "A" and the run was repeated. The difference in the adsorption curves allowed us to calculate the amount of hydrogen adsorbed as a function of pressure.

Modeling

Two modeling projects were performed to help understand the storage capability of modified graphites and nanostructured carbons. A semi-empirical quantum chemical study of hydrogen intercalation into modified graphites was performed along with molecular dynamic studies of hydrogen transport through carbon nanotubes.

Results and Discussion

Aerogel Structure-Property Relationships

The structure and properties of RF-derived carbon aerogels are largely controlled by the [Resorcinol]/[Catalyst] (R/C) ratio of the starting solution. At R/C=50, carbon aerogels have particle diameters on the order of 7-9 nm with specific surface areas of ~800 m^2/g. In this type of aerogel, the particles are well-interconnected with the neck size approaching the particle diameter. In contrast, carbon aerogels synthesized at R/C=200, have lower surface areas (~600 m^2/g) and smaller necks between spherical particles of ~12 nm diameter. Interestingly, the specific surface area of these carbon aerogels is practically independent of the bulk density for samples prepared *at the same R/C ratio* [Pekala 1995]. Thus, RF-derived carbon aerogels with a higher bulk density simply have more interconnected particles per unit volume than their low density counterparts. In the case of the PF-derived carbon aerogels, specific surface area (~500 m^2/g) is also found to be largely independent of density at a given catalyst level [Pekala, in press].

Transmission electron micrographs of RF-derived carbon aerogels reveal an interconnected fibrous structure at R/C=50 whereas distinct spherical particles are observed at R/C=200. These structures have been explained in terms of the initial sol-gel chemistry and solution thermodynamics [Gebert 1994; Pekala 1992]. The PF-derived carbon aerogels reveal interconnected platelets of irregular shape with characteristic sizes of 10-15 nm. Figure 2 shows representative TEMs for the carbon aerogels derived from different precursors.

Raman spectroscopy was performed on carbon aerogels to probe the internal structure of the interconnected particles or platelets. In both cases, a Raman-allowed E_{2g2} peak was observed near 1580 cm^{-1} (designated as the*G* band) while a Raman line attributable to in-plane disorder was observed near 1360 cm^{-1} (the *D* band). The in-plane microcrystallite size L_a was estimated from Knight's empirical formula, $L_a = 44 (I_G/I_D)$. For RF-based carbon aerogels pyrolyzed at 1050 °C, L_a is approximately 25 Å, independent of the bulk density or R/C ratio. For PF-based carbon aerogels pyrolyzed under the same conditions, L_a ranges from 25-35 Å with a slight density dependence. In both cases, the Raman data suggest that 25-35 Å wide graphene sheets are the underlying units in the carbon aerogel structure. The size of these units is largely independent of the sol-gel polymerization conditions and precursor chemistry; however, L_a is sensitive to heat treatment temperature [Fung 1993; Reynolds 1994].

Table 1. Hydrogen Adsorption at 77K

Aerogel Composition	Aerogel density (g/cm^3)	Pyrolysis Temp (^{o}C)	H_2(wt.%)	H_2(kg/m^3)
RF-derived CARBON	0.149	1050	5.87	9.3
RF-derived CARBON	0.284	1050	3.56	10.5
RF-derived CARBON	0.637	1050	3.19	21.0
PF-derived CARBON	0.422	1050	2.12	9.1
PF-derived CARBON	0.547	1050	2.25	12.6
PF-derived CARBON	0.742	1050	1.46	11.0
RF	0.106	—	16.75	21.3
RF	0.193	—	4.5	9.1
RF	0.411	—	4.4	19.0

Because of the *high volumetric surface areas* that can be achieved in aerogels, it was hoped that they would enable us to meet the DOE volumetric energy density requirement for hydrogen storage (62 kg H_2/m^3). In our previous report, we found that hydrogen was quickly adsorbed onto aerogels at relatively low pressures. A plateau value was reached for carbon aerogels by 500 psi. In some resorcinol-formaldehyde (RF) aerogels, hydrogen adsorption continued to increase with pressure. Figure 3 shows the adsorption profile for an RF aerogel having a bulk density of 0.106 g/cm^3. This samples adsorbs 16.8 wt % hydrogen at 77 K and 1000 psi. The highest value achieved in carbon aerogels was 5.9 wt. % under similar conditions. Based upon these results, we investigated the dependence of hydrogen adsorption upon aerogel density. Table 1 outlines the data for RF and carbon aerogels. In general, the specific hydrogen adsorption decreases as the aerogel density increases. Our original hypothesis assumed that the high *volumetric surface areas* achievable in aerogels would enable us to approach the DOE volumetric energy density requirement of 62 kg H_2/m^3. To date, the highest volumetric adsorption values that we have achieved are only 20-24 kg H_2/m^3 at 77 K. These data suggest that aerogels have limited utility for hydrogen storage.

Modeling

For the quantum chemical study two parallel coronene molecules (Figure 4) were used as a model of graphite. These are polyaromatic rings with twenty four carbons each.. This molecule was chosen as the largest molecular cluster model that could be handled with existing computer power. In order to create different environments, the coronene's hydrogens were replaced by the series F, Cl, Br, I, OH, NH_2, CH_3, SH, PH_2. This provides a data set of ten molecules . On each of these molecules, the geometry of the complex was varied to find the configuration with the lowest energy. A hydrogen molecule was placed in the center directly between the two substituted coronenes and the geometry optimized again. In the simplest cases, these calculations can be thought of as giving us three pieces of information - the initial preferred interplanar distance, the preferred interplanar distance with the H_2 in between and the energy change. The calculations were performed using the MOPAC semi-empirical quantum chemical package.

The results of these calculations yield information on several aspects of the nature of hydrogen intercalation. One question that is answered immediately is that the hydrogen molecule does not dissociate into atomic hydrogen in any of the modified graphitic environments. The way the substituents affect the system seems to depend mostly on their size and the degree to which they cause distortion of the planarity of the coronene. For H, F, Br, OH, SH, and PH_2 sustituents the coronenes essentially remained planar and the effect of substitution was to change the preferred initial separation. Introduction of a H_2 molecule always led to an increase in the separation and some increase in the total energy of the complex. This is shown in Figures 4 for unsubstituted coronenes. The trend in this set was that the larger the initial separation, the larger the change in the distance but at a smaller energy cost. For Cl, I, CH_3, and NH_2 substituents, considerable distortion occurs in the coronene. The CH_3 systems, with and without the H_2, are shown in Figure 5. The major cause of distortion was steric interaction between bulky substituents, although in the case of the halogens the interplay between electronic interactions (weakening ring bond strength) and steric interactions is important. For these compounds introducing the interplanar hydrogen can have unusual effects, even allowing the highly distorted molecules to find lower energy structurres.

The second set of calculations are ongoing and they are classical molecular dynamics calculations of H_2 diffusing through carbon clusters of various forms. The intention is to calculate the diffusion constants for H_2 in amorphous and nanostructured environments. We have written programs to construct carbon nanotubes (Figure 6) and have modified existing molecular dyanmics packages to allow the carbon to be either a rigid matrix or to have thermal vibrations. As the rigid calculations are orders of magnitude faster, they are being used to get longtime diffusivities while the thermal calculations are used to understand the short time dyanmics in greater detail.

Future Work

The aerogel synthesis and characterization efforts have been terminated; however, a modest level of computer modeling will continue into the future.

Acknowledgments

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Figure Captions

Figure 1.	Schematic diagram of hydrogen adsorption apparatus.
Figure 2.	Transmission electron micrographs of carbon aerogels derived from (a) resorcinol-formaldehyde [R/C=200] precursor and (b) phenolic-furfural precursor. Both samples were pyrolyzed at 1050 °C under flowing nitrogen.
Figure 3.	Adsorption isotherm (77 K) for resorcinol-formaldehyde aerogel having a bulk density of 0.106 g/cm^3. The sample was synthesized at R/C=200.
Figure 4.	Depiction of two coronene molecules (a) before and (b) after hydrogen insertion.
Figure 5.	Depiction of two methyl-substituted coronene molecules (a) before and (b) after hydrogen insertion.
Figure 6.	Computer model of a carbon nanotube.

Adsorption Apparatus

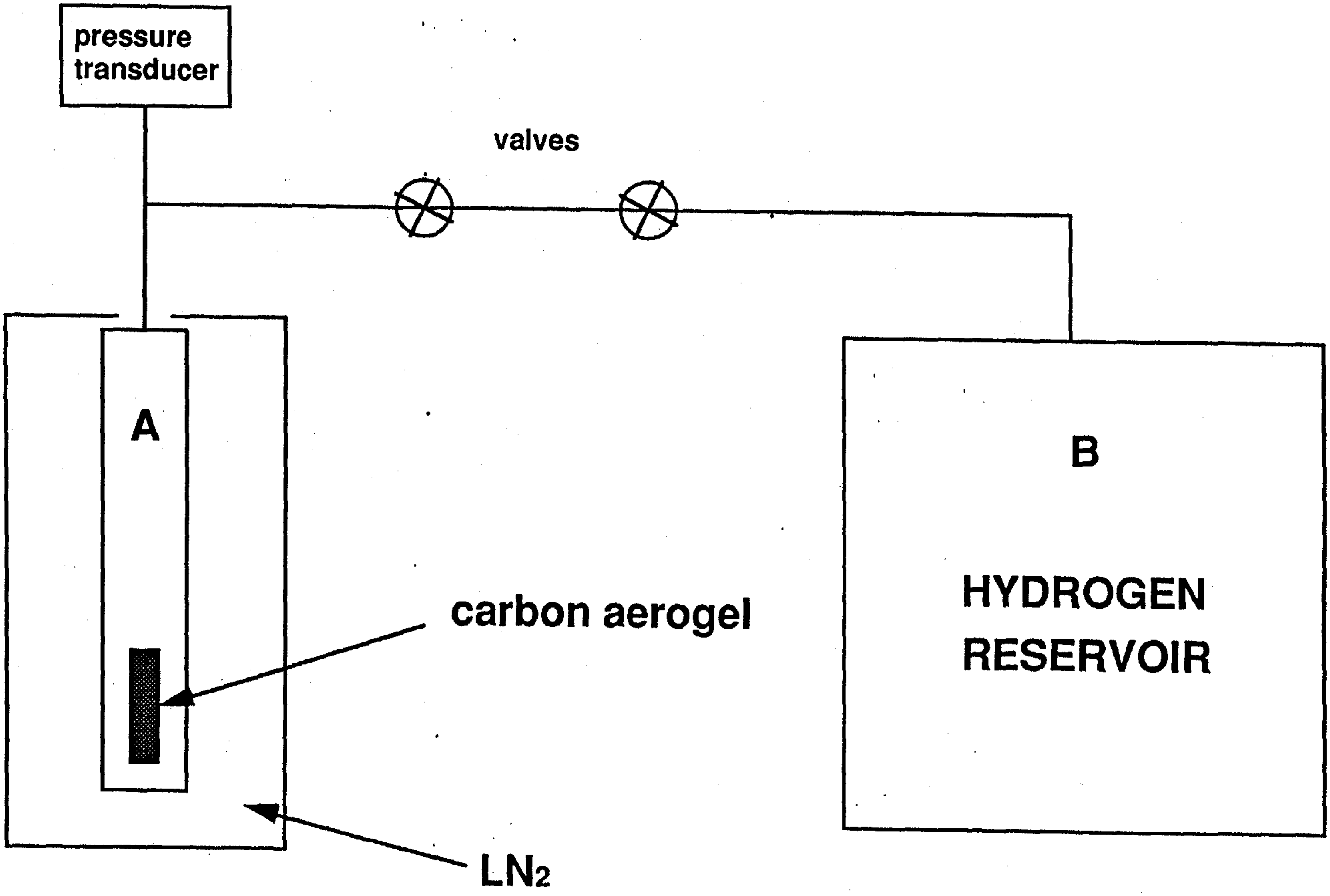


Figure 1

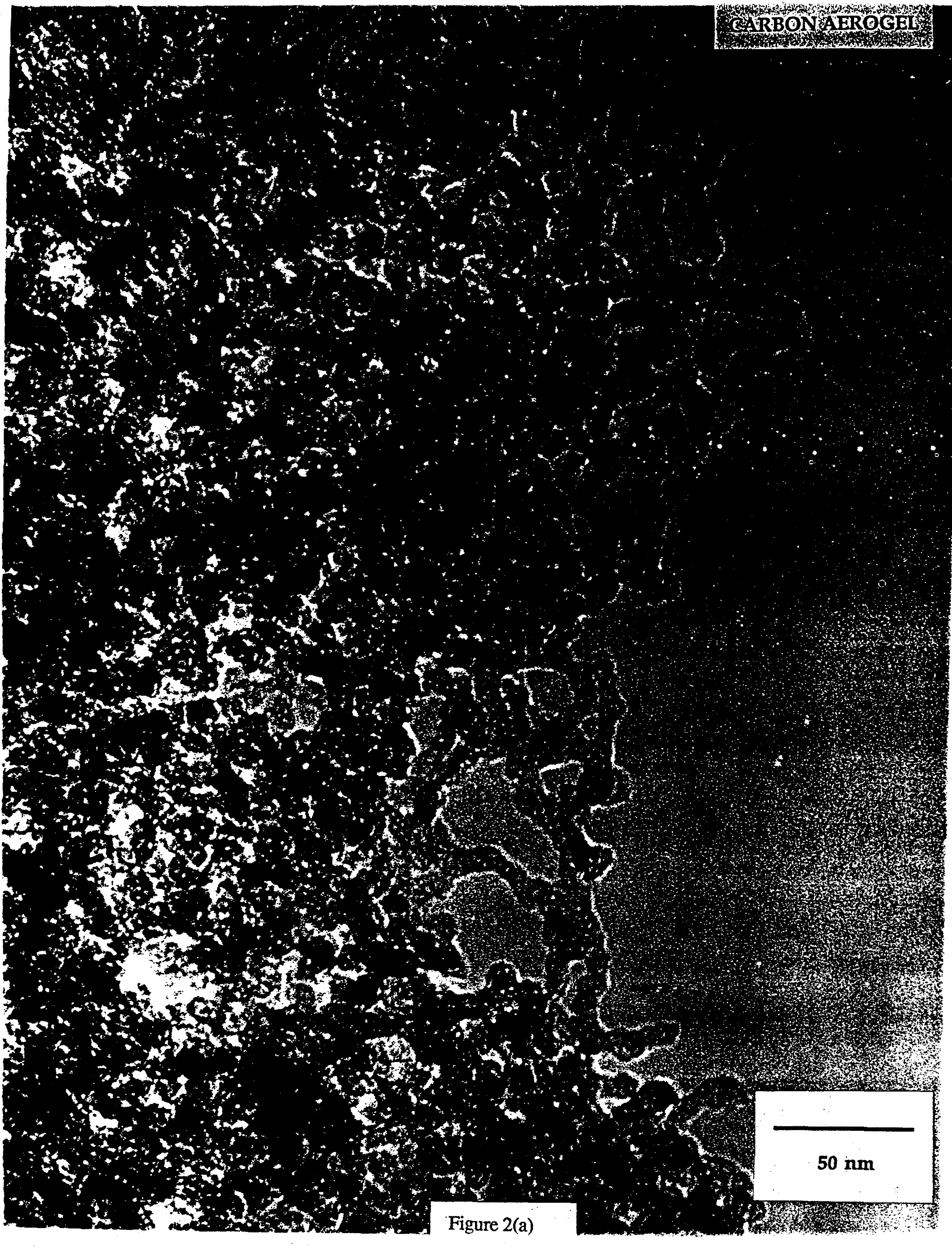


Figure 2(a)

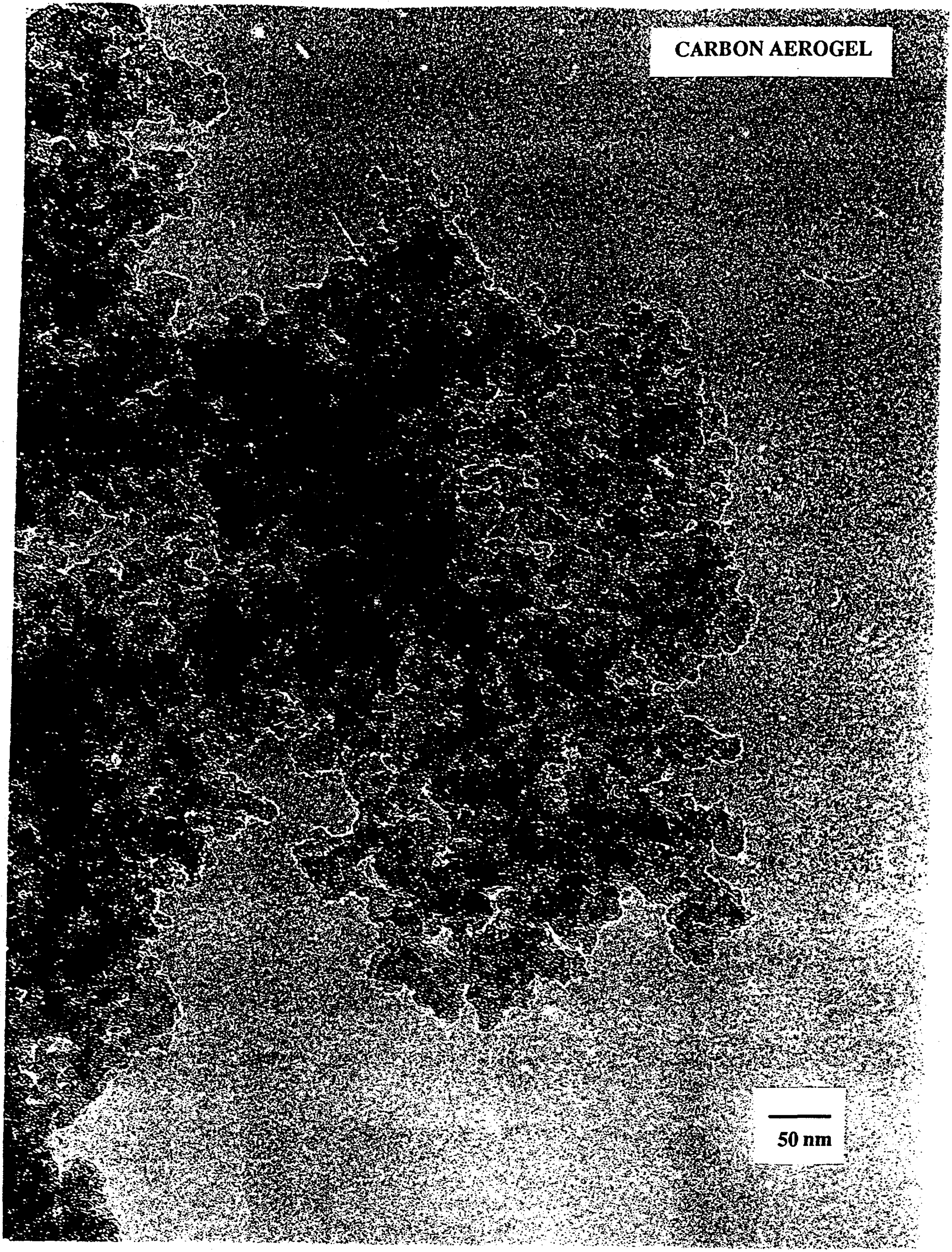
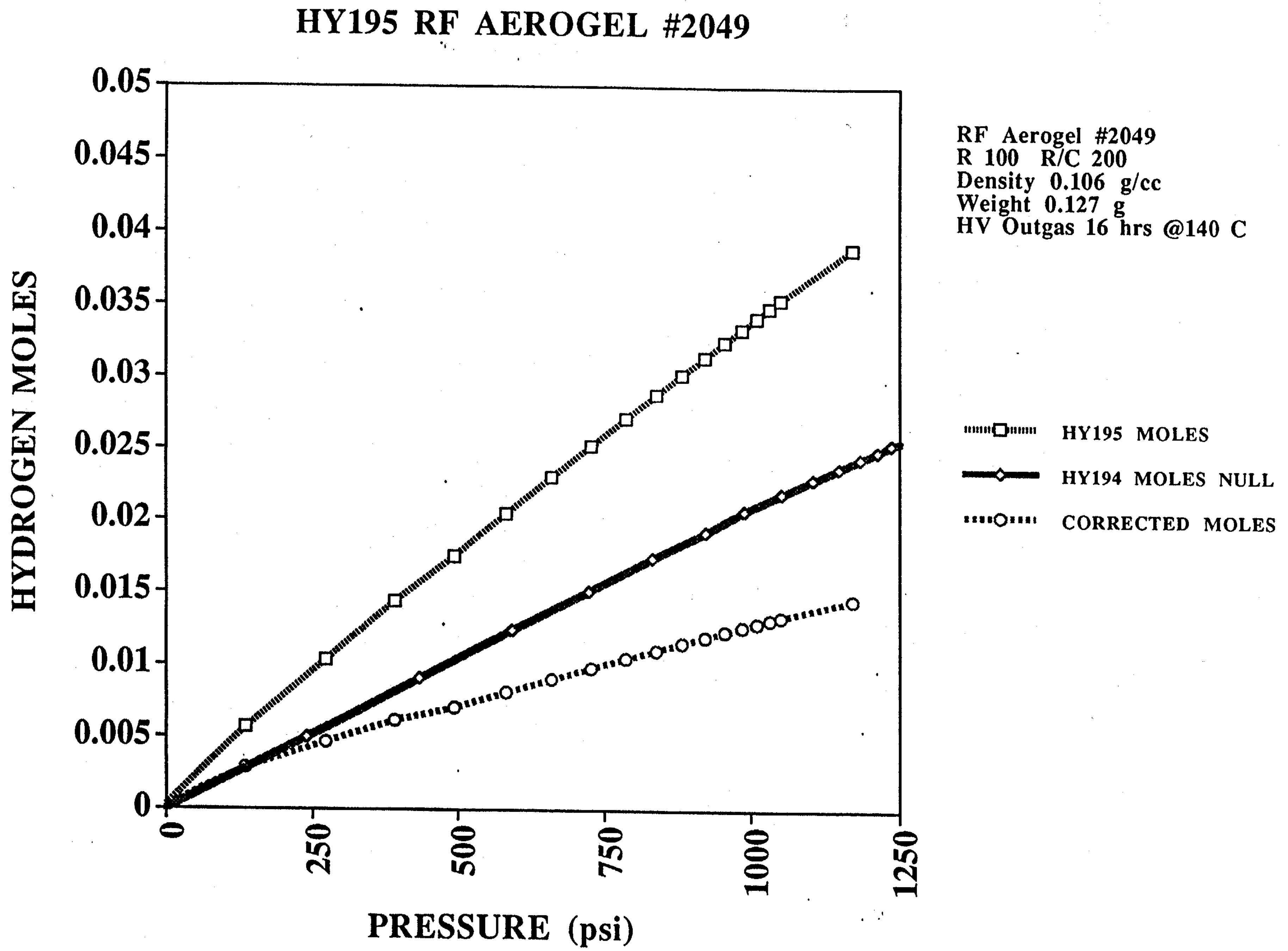


Figure 2(b)


HY195 RF AEROGEL #2049
HYDROGEN MOLES
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0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
PRESSURE (psi)
0
250
500
750
1000
1250
RF Aerogel #2049
R 100 R/C 200
Density 0.106 g/cc
Weight 0.127 g
HV Outgas 16 hrs @140 C
HY195 MOLES
HY194 MOLES NULL
CORRECTED MOLES

Figure 3

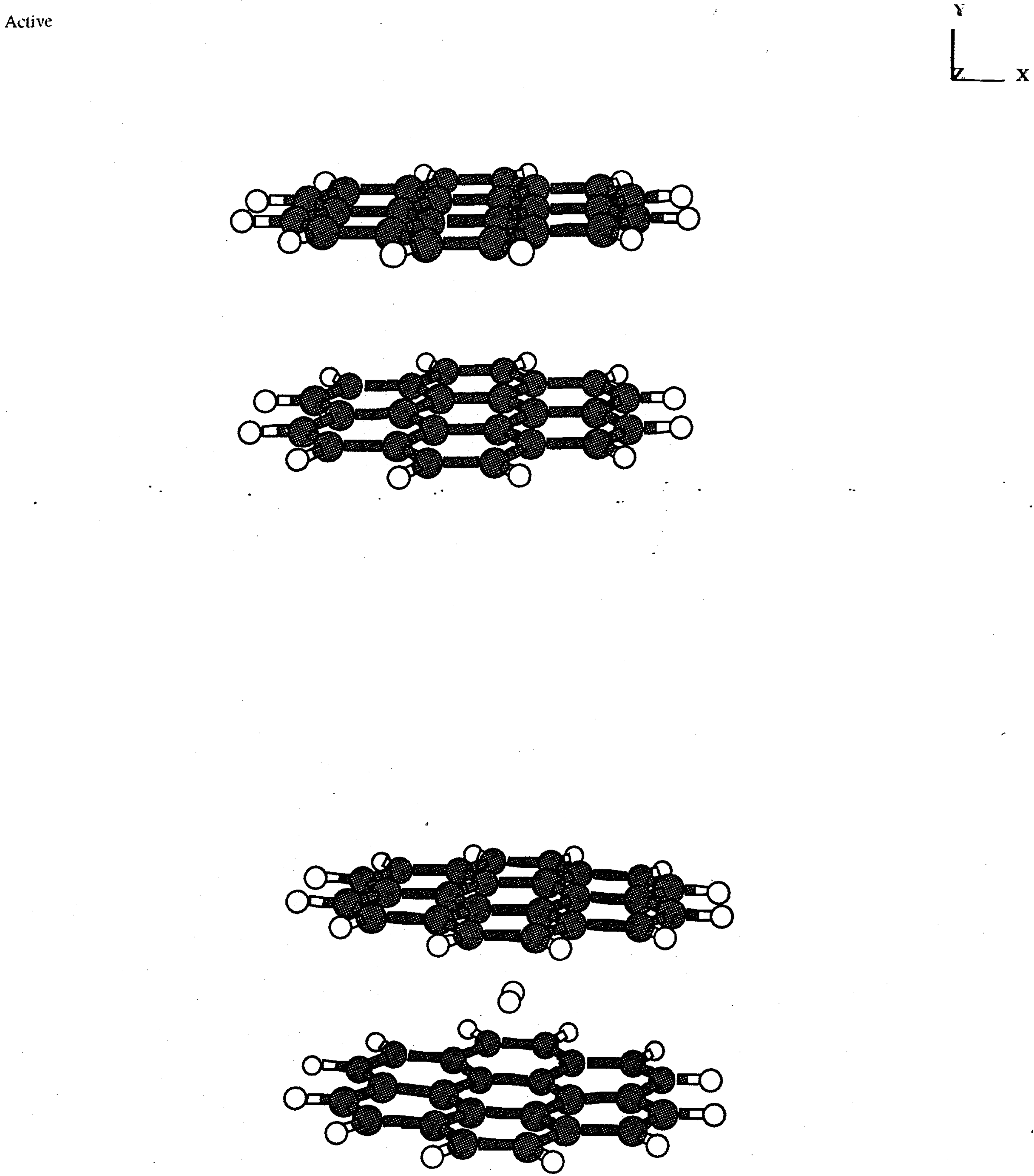

Figure 4

Active

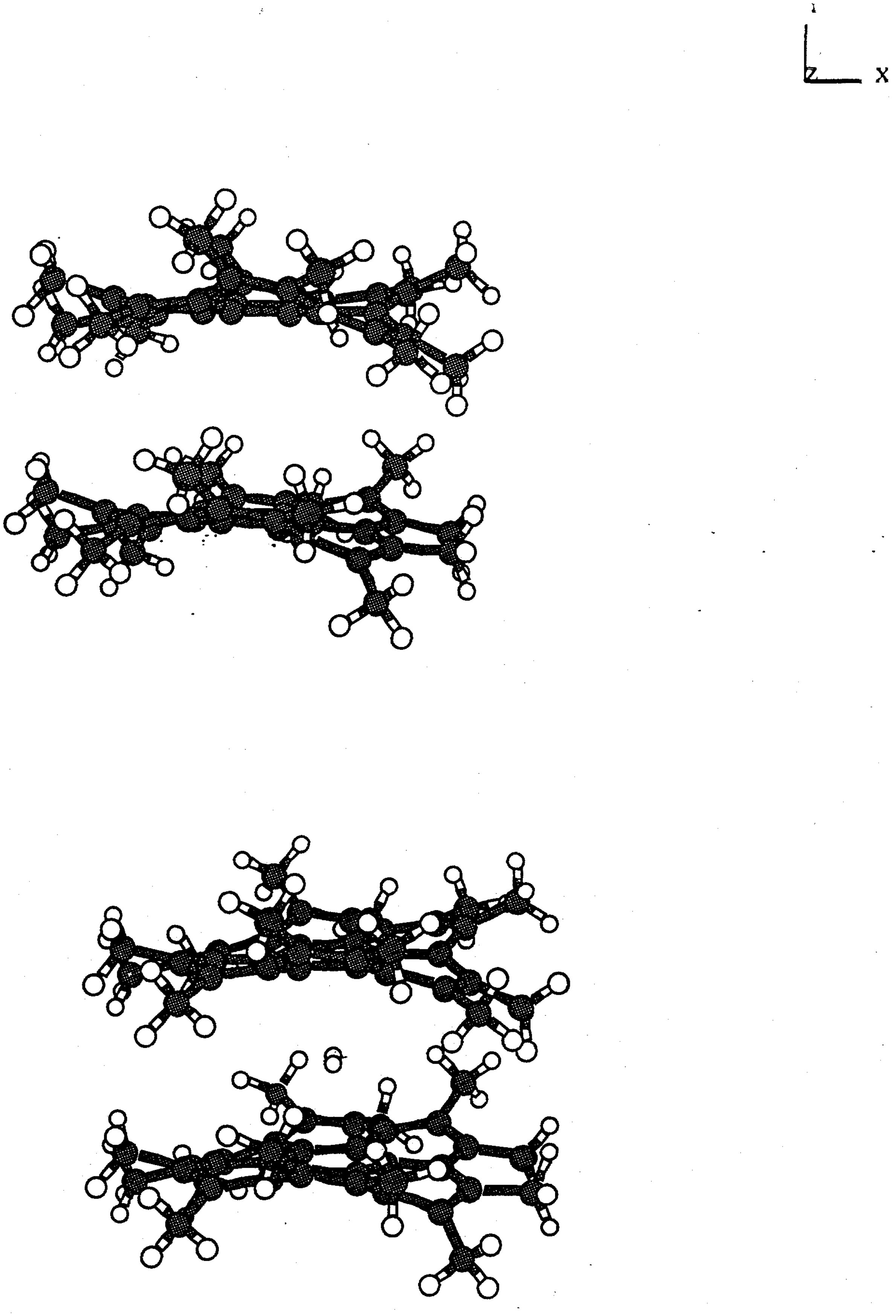

Figure 5

Active

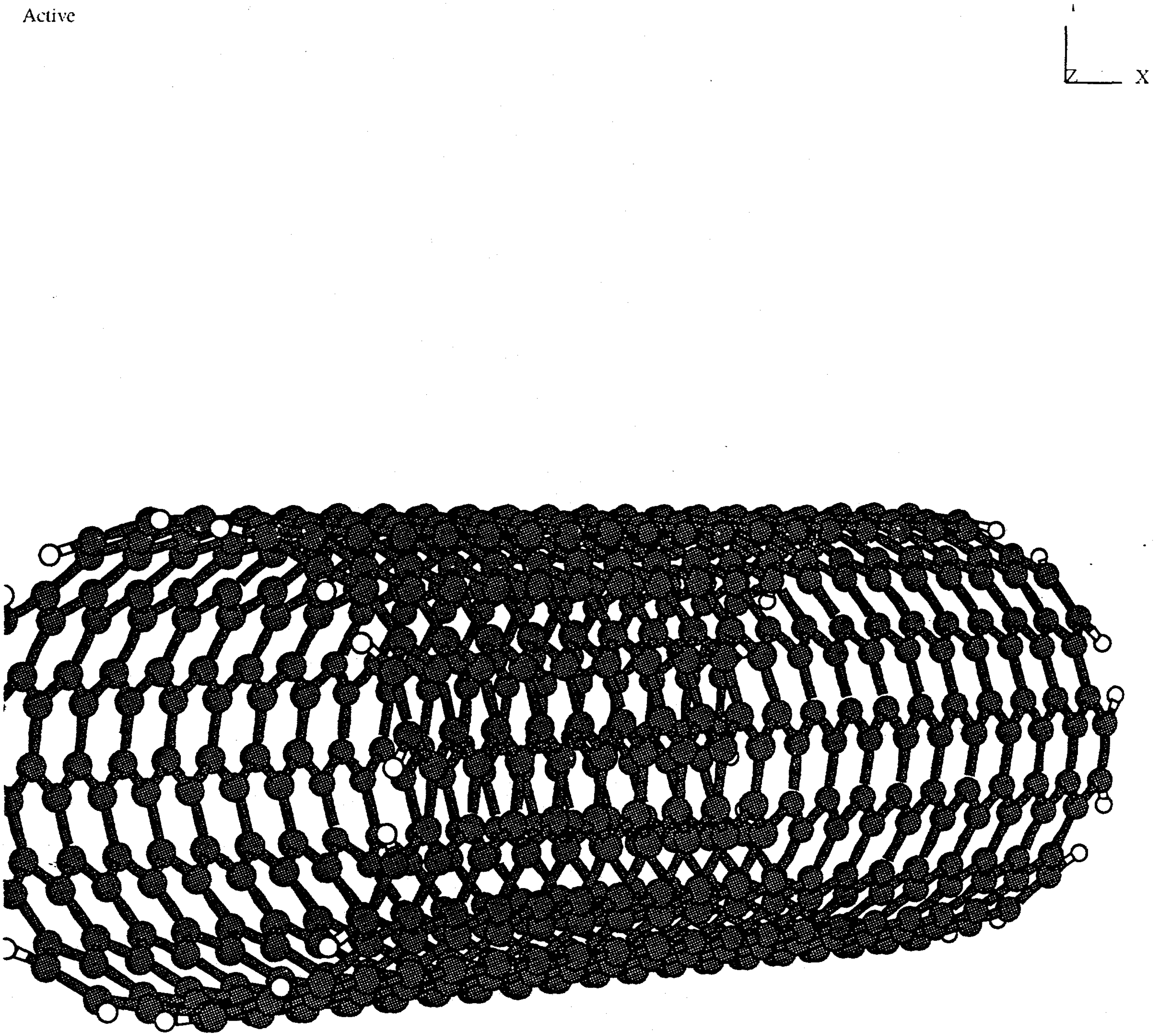

Figure 6