

Hydrogen Uptake in Cluster-Assembled Carbon Thin Films: Experiment and Computer Simulation

P. Piseri, E. Barborini, M. Marino,[†] and P. Milani*

INFN-Dipartimento di Fisica and CIMAINA, Università di Milano, via Celoria 16, I-20133 Milano, Italy

C. Lenardi

INFN-Istituto di Fisiologia Generale e Chimica Biologica and CIMAINA, Università di Milano, via Trentacoste 2, I-20134 Milano, Italy

L. Zoppi and L. Colombo

INFN DEMOCRITOS National Simulation Center and Dipartimento di Fisica, Università di Cagliari, I-09042 Monserrato (CA), Italy

Received: October 17, 2003; In Final Form: January 15, 2004

X-ray absorption measurements and large-scale molecular dynamics simulations are used to investigate the storage capacity of hydrogen in cluster-assembled carbon films. Experimental results show that nanostructured carbon exposed to H₂ at 0.12 MPa for 3 h at room temperature can store up to 1.5 wt % of hydrogen. These experimental results are in good quantitative agreement with the computational data. Both experiments and simulations confirm that hydrogen is chemisorbed on the carbon. The simulations provide information about the spatial distribution of the sorption sites of atomic and molecular hydrogen.

The study of the interaction of hydrogen and carbon has been a very active field of research since the beginning of the last century.^{1,2} It has been shown that the principal mechanism of hydrogen uptake on carbon surfaces is chemisorption even at room temperature.^{2,3} The process involves different sites, such as carbon atoms situated at the edge or corners of sp² domains,² dangling bonds,⁴ and reconstructed regions.⁵

Carbon-based sorbents have also been characterized in view of applications requiring efficient hydrogen storage.⁶ Marginal improvements have been reported compared to the performances of other storage systems.⁶

Recently, a considerable experimental and theoretical effort has been directed toward the investigation of nanostructured carbon in the form of nanotubes,^{7–12} fibers,¹³ and mechanically milled graphite⁴ as hydrogen sorbents. The initial enthusiasm for the reported extraordinarily large amount of hydrogen stored in nanotubes has been replaced by skepticism because of the irreproducibility of the first reports and the high number of contradictory results published so far.^{9,10}

Many fundamental aspects governing the interaction of hydrogen with nanostructured carbons are still waiting to be clarified. The two most important ones for the assessment of hydrogen storage capability are the interplay between chemisorption and physisorption¹³ and the role played by the nanoscale structure (local curvature, dangling bonds, hexagonal rings) in the hydrogen-uptake process.¹⁴ Moreover, the availability of experimental methods capable of avoiding artifacts in the evaluation of the quantity and the chemical status of the adsorbed and released hydrogen is still a matter of debate.¹⁰

Cluster-assembled nanostructured carbon (ns-C) has been shown to be an interesting system for hydrogen uptake.¹⁵ We

have proved that the nano- and mesostructure, the porosity, and the dominant hybridization character of C–C bonds as well as the density of ns-C systems can be tailored according to demand by varying the precursor cluster mass distribution.^{16–18} The structure on the nanoscale results in an extraordinarily large value for the specific area available for the physis- and/or chemisorption of hydrogen species,¹⁵ making ns-C an interesting playground for the investigations aimed at quantitatively understanding and predicting the hydrogen-uptake capacity of novel nanostructured carbon systems.

In our previous thermally programmed desorption mass spectroscopy (TPD/MS) characterization of ns-C films exposed to molecular hydrogen, we observed a peak at about 230 °C attributed to the population of physisorbed hydrogen sites and a steep exponential slope over 500 °C attributed to the desorption of chemisorbed hydrogen.¹⁵ Recent analogous measurements on carbon nanostructures^{19,20} show very similar behavior for comparable heating rates. The second rise in desorption is interpreted as hydrogen weakly bonded to carbon and is considered to be of fundamental importance to hydrogen-storage properties. Hydrogen absorption appears to be favored by the presence of defect structures; however, the nature of the bonding is ill-defined.

In this letter, we report the results obtained by a combination of real and virtual experiments aimed at the investigation of the nature of the interaction and bonding of hydrogen with cluster-assembled carbon and the role of the nano- and mesostructure.

We have grown nanostructured carbon films with thicknesses ranging from 0.5 to 1 μm by depositing on a silicon substrate a supersonic cluster beam produced by a pulsed microplasma cluster source.²¹ The apparatus and deposition procedure are described in detail in ref 22. The cluster mass distribution was

* Corresponding author. E-mail: paolo.milani@mi.infn.it.

[†] Present address: Dipartimento di Matematica, Università di Milano, via Saldini 50, 20133 Milano, Italy.

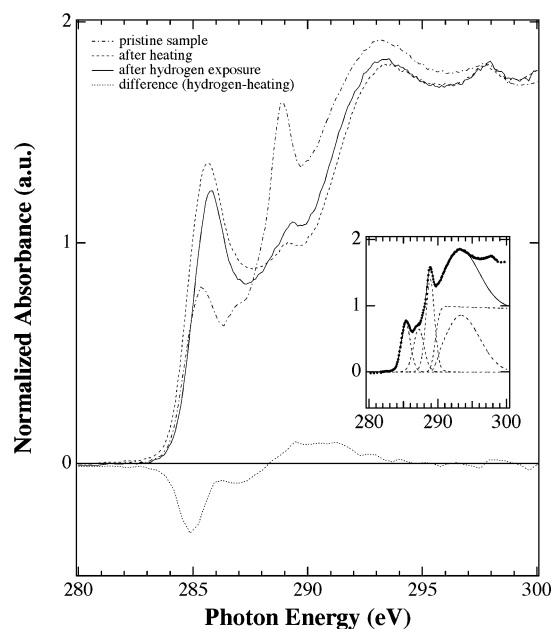


Figure 1. Carbon K-edge spectra of ns-C films. (· · ·) As deposited; (---) after heating (400 °C for about 1 h in UHV); (—) after hydrogen exposure (0.12 MPa for 3 h at room temperature). (Bottom) difference spectrum between the spectra after heating and after hydrogen exposure. (Inset) fitted peaks in the near-threshold region: three pseudo-Voigt functions in the subthreshold region, an asymmetric Gaussian function describing the main peak above the threshold, and a modified erf function representing the step at the ionization threshold. All of the spectra can be conveniently fitted by assuming an ionization potential close to 289.4 eV.

log-normal in the range of 0–2000 atoms/cluster peaking at about 400 atoms/cluster.

The effects of hydrogen exposure have been characterized by near-edge X-ray absorption fine structure spectroscopy (NEXAFS) using the Super-ACO/CLIO beamline SA72 at the synchrotron radiation facility LURE in Paris. The samples were exposed to molecular hydrogen (purity 99.9999%) at a pressure of 0.12 MPa for 3 h at room temperature inside the preparation chamber (base pressure $< 5 \times 10^{-10}$ Torr) of the spectroscopic apparatus. The energy resolution was 0.2 eV at the carbon K-edge. The spectra have been recorded in total electron yield (TEY) mode. The samples have been mounted at the “magic angle” to eliminate the dependence of the spectra on the polarization of the X-ray source.

The normalized carbon K-edge NEXAFS spectra of cluster-assembled carbon films are shown in Figure 1. In the subthreshold region, two main features are easily recognizable: the peak related to the π^* C=C transition, located at about 285.3 eV, and the peak associated with the σ^* C–H transition at about 288.7 eV.^{23,24} The large σ^* C–H resonance in the as-deposited sample originates from the dissociation of physisorbed species containing hydrogen, mainly water, and hydrocarbons. After heating (400 °C for about 1 h in UHV), the σ^* C–H is strongly reduced. The treatment induced a partial graphitization of the films, leading to a more intense and wide π^* C=C peak, from which the increment of the sp^2 fraction has been estimated (about 80% sp^2 after heating with respect to 60% sp^2 before heating). Subsequent exposure to pure hydrogen has the effect of partially restoring the σ^* C–H peak and narrowing the π^* C=C resonance. The hydrogen absorption is always accompanied by a decrease in the height and fwhm of that peak with a corresponding loss of sp^2 sites. In fact, the sp^2 fraction decreases to about 0.7. The actual absence of oxygen-containing species after annealing and hydrogen exposure is monitored by the

strong reduction of any features at the O K-edge NEXAFS spectra. Thus, because water contamination is negligible, the process of annealing and hydrogen sorption from direct H_2 exposure can be iterated.

The quantitative evaluation of hydrogen uptake has been obtained from a peak-fitting procedure of the photoabsorption spectra after an accurate calibration and normalization of the experimental NEXAFS curves. Because of the highly local character of the core excitations, it is reasonable to assume that the area of the σ^* C–H peak is directly related to the amount of H chemically bonded to C. This assumption is supported by the analysis of absolute oscillator strengths of gas-phase hydrocarbon molecules obtained from dipole regime inner-shell electron energy loss (ISEELS) spectra reported by Hitchcock and Mancini.²⁵

We have fitted their oscillator-strength curves as the superposition of a modified erf function, representing the step at the ionization threshold, and a suitable set of pseudo-Voigt functions representing the peaks in the subthreshold region. For this purpose, we have developed a series of routines written in MATLAB language.²⁶ The areas of the π^* and σ^* C–H peaks (normalized with respect to the area of a fixed larger portion of the spectra) as functions, respectively, of the number of carbon–carbon and carbon–hydrogen bonds per C atom present in the molecule of each hydrocarbon have been found to follow a linear relationship. We have determined by linear regression the two proportionality factors, and we have assumed that their ratio is also the same for ns-C samples. In this way, if the number of carbon–carbon bonds in a given sample is known, then the corresponding quantity of chemisorbed H can be easily determined from the ratio of the σ^* C–H and π^* C=C peak areas.

We applied the method to our NEXAFS spectra by performing an analogous fit (see the inset in Figure 1) and then by determining the π^* C=C bonds content (i.e., the sp^2 fraction, according to the criterion already proposed by Fallon et al.)²⁷ The hydrogen uptake has then been quantified from the area of the fitted C–H* peak. Following this procedure, the total amount of chemisorbed hydrogen after molecular hydrogen exposure was evaluated to be about 1.5 wt %. It should be pointed out that, although the loading conditions have been not particularly severe, the quantity of absorbed hydrogen is sizable. In any case, the hydrogen-storage kinetics appears to be rather slow, as for other carbon sorbents.^{2,3} This characterization shows that the more significant amount of the detected hydrogen comes from the direct exposure to H_2 and that only a minimal part comes from residual contaminants. It should also be stressed that from NEXAFS measurements it is possible to reveal only the chemisorbed hydrogen. The illustrated procedure represents a novel route to the quantification of the chemisorbed hydrogen in carbon-based specimens.

As for computer modeling, it has been proven that large-scale molecular dynamics simulations (MD), which are based on empirical Tersoff-like interatomic potentials, are quite accurate in reproducing both the SCBD process¹⁶ and the atomic hydrogen incorporation into ns-C films.²⁸ In this work, therefore, we at first extended the simulation of SCBD growth up to an unprecedented system size so as to produce a computer sample large enough to correctly reproduce nanoporosity and matrix mass density fluctuations as well as all of the possible local carbon environments offered to atomic and molecular hydrogen.

The typical computer-generated sample contained up to 12 000 carbon atoms, deposited on a (001) diamond substrate. The simulated cluster beam had a mass distribution similar to

that of real experiments. The clusters were deposited with an energy as low as 0.1 eV/atom so as to prevent cluster fragmentation during landing. After deposition, the system was aged at 2000 K for 25 ps (1 time step = 0.5×10^{-15} s). Overall, its structural properties have been found to be in nice agreement with experimental knowledge: ~ 1 g/cm³ mass density and more than a 70% occurrence of sp² bonds (dominant graphitic-like character).

The hydrogen-storage process has been simulated by exposing the ns-C computer-generated sample to an external atmosphere of H₂ gas at different values of temperature and pressure. This process was simulated by means of grand canonical Monte Carlo (GCMC) runs, where the interatomic interactions were modeled by means of a generalized Lennard-Jones functional^{29,30} whose reliability has been recently proven for similar investigations.³¹ More specifically, after the simulation of the SBCD growth (see above), the nanocarbon matrices have been considered to be static hosts, whereas the hydrogen molecules have been modeled as rigid units. The dispersive molecular (i.e., H₂-H₂) as well as molecule-host (i.e., H₂-ns-C) interactions were described by means of (12-6) Lennard-Jones potentials, with $\epsilon = 36.7$ K and $\sigma = 2.958$ Å for H₂-H₂; as for C-C interactions, we set $\epsilon = 28.2$ K and $\sigma = 3.40$ Å. Finally, the H₂-C parameters have been derived according to the usual Berthelot rules (i.e., $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ and $\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{1/2}$ with A,B=C or H₂).

GCMC simulations allowed for the computation of the isothermal adsorption curves, providing direct quantitative information on either the gravimetric or volumetric density of molecular hydrogen as a function of the ns-C matrix temperature and the pressure of the external H₂ atmosphere.

By applying the above simulation protocol to differently grown ns-C films, we observed that the actual nanostructure does not sizably affect the net amount of stored H₂. For instance, at an external pressure of 12.5 MPa and $T = 300$ K, we estimate a volumetric density of about 10 kg H₂/m³ in most cases. However, the system temperature was found to play a more important role: by cooling from room temperature down to $T = 77$ K, we observed an ~ 5 -fold increase in the volumetric density of stored H₂. Moreover, we observed that the estimated pressure at which H₂ storage is more efficient in ns-C structures than in the free volume was high, namely, between 12 and 18 MPa. This result seems to indicate that such systems could not be considered to be efficient materials for H₂ storage. Furthermore, when the simulation results are cast in terms of weight percent of stored hydrogen, we can estimate a negligibly small value of physisorbed hydrogen at the typical experimental pressure (<1 MPa) and temperature (300 K).

The key point of the GCMC simulations is that so far the sole physisorption mechanism was included. To carry out a more realistic simulation so as to compare simulations to the present NEXAFS characterization, we need to consider both physisorption and chemisorption mechanisms.

To this aim, we have set up a 2-fold computational strategy. At first, by following the same molecular dynamics procedure elaborated in ref 27, we have evaluated the hydrogen chemisorption process of ns-C matrices as obtained by the random insertion of atomic hydrogen. At this stage, empirical Tersoff-like potentials for C-H and H-H interactions have been adopted. The random insertion of H atoms has been completed by very long (160-ps) thermal annealing so that the excess amount of atomic H was in fact desorbed through the free surface. Then the hydrogenated ns-C:H matrices have been

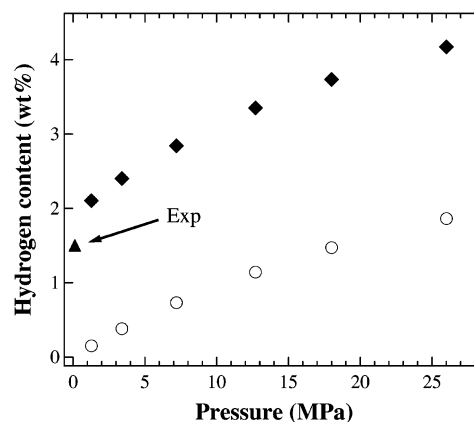


Figure 2. Theoretical (♦) and experimental (▲) estimations of the hydrogen weight occurrence (wt %) at room temperature. (○) Contribution to the hydrogen content due to the physisorption mechanism only.

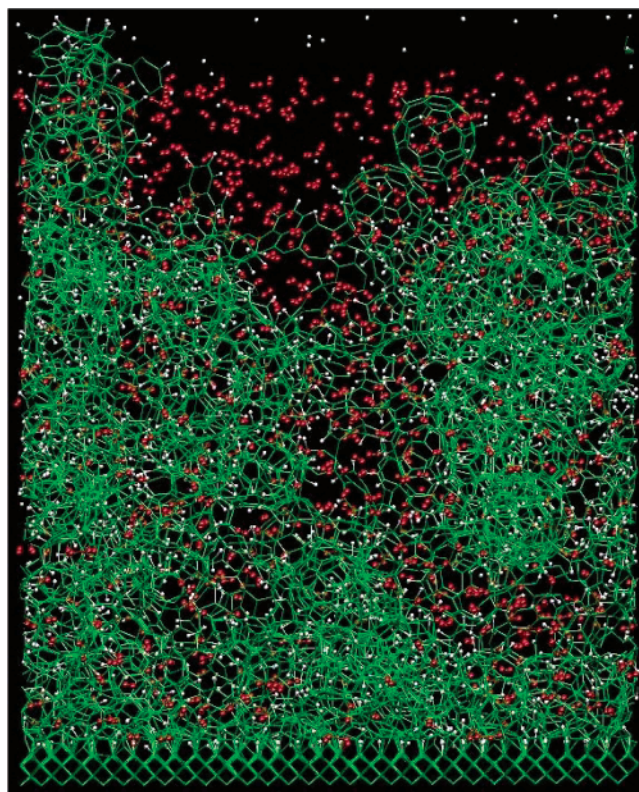


Figure 3. Atomic structure of a hydrogenated ns-C film as obtained by a direct molecular dynamics simulation of film growth, physisorption, and chemisorption processes. (Green sticks) C-C bonds of the grown ns-C film (whose C atoms are not displayed); (white balls) chemisorbed hydrogen atoms; (red balls) physisorbed hydrogen molecules. For details, see the text.

exposed to an H₂ atmosphere, following a similar GCMC procedure to that described above.

In Figure 2, we report the theoretical predictions for hydrogen weight occurrence when both physisorption and chemisorption mechanisms are present (solid diamonds) and when just H₂ storage is simulated (open symbols) at $T = 300$ K. Present experimental data are reported as well (solid triangle). It is apparent from Figure 2 that chemisorption plays a major role. The agreement between theory and simulation is excellent: the estimated theoretical weight occurrence at experimental conditions is about 1.8 wt %, to be compared with the 1.5 wt % value.

Such quantitative agreement heuristically proves that the present theoretical picture is overall trustworthy, although the

interatomic potentials here adopted for both GCMC and MD simulations can hardly describe the details of the C–H chemical bonding on quantitative grounds. The same agreement makes us confident of the reliability of the present computer experiments to provide valuable additional information. For instance, we can investigate the actual space distribution of H and H₂ species, as reported in Figure 3 as white and red symbols, respectively. This snapshot (referring to a system containing 7092 C atoms, 2000 H atoms, and 880 H₂ molecules) clearly proves that H₂ storage preferentially occurs in the low-density regions (i.e., within the cavities offered by the underlying porous structure) of the ns-C film, whereas hydrogen chemisorption mainly concerns the (amorphous) graphitic-like network of C–C bonds. This compares well with the behavior observed for different nanostructured carbon systems.³⁰

In conclusion, we have characterized both experimentally and theoretically the hydrogen uptake of cluster-assembled carbon films. In particular, using NEXAFS spectroscopy we have developed a method for a quantitative evaluation of hydrogen uptake. Our results show that nanostructured carbon films exposed at 0.12 MPa for 3 h at room temperature can store up to 1.5% of hydrogen in weight. This estimation is consistent with theoretical predictions based on a direct atomic-scale simulation of both ns-C film growth and hydrogenation. Furthermore, the combined analysis of the present experimental data and atomistic simulations seems to indicate that the main mechanism responsible for H storage is chemisorption, whereas physisorption plays a minor role. Finally, it is found that ns-C porosity favors the accumulation of H₂ species, whereas atomic hydrogen is mainly responsible for the decoration of internal surfaces (i.e., saturation of carbon dangling bonds).

Acknowledgment. We acknowledge partial financial support from Project FIRB. We thank C. Laffon and Ph. Parent for their technical support at the LURE facility.

References and Notes

- (1) Bangham, D. H.; Stafford, J. *J. Chem. Soc.* **1925**, 127, 1085.
- (2) Bansal, R. C.; Vastola, F. J.; Walker, P. L., Jr. *Carbon* **1971**, 9, 185, and references therein.
- (3) *Carbon Black: Science and Technology*; Donnet, J. B., Bansal, R. C., Wang, M. J., Eds.; Dekker: New York, 1993.
- (4) Orimo, S.; Majer, G.; Fukunaga, T.; Züttel, A.; Schlapbach, L.; Fujii, H. *Appl. Phys. Lett.* **1999**, 75, 3093.
- (5) Miura Y.; Kasai, H.; Diño, W.; Nakanishi, H.; Sugimoto, T. *J. Appl. Phys.* **2003**, 93, 3395.
- (6) Hynek, S.; Fuller, W.; Bentley, J. *Int. J. Hydrogen Energy* **1997**, 22, 601.
- (7) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, J. *Nature* **1997**, 386, 377.
- (8) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, 286, 1127.
- (9) Hirscher, M.; Becher, M.; Haluska, M.; Dettlaff-Weglikowska, U.; Quintel, A.; Duesberg, G. S.; Choi, Y. M.; Hulman, M.; Roth, S.; Stefanek, I.; Bernier, P. *Appl. Phys. A* **2001**, 72, 129.
- (10) Züttel, A.; Orimo, S. *MRS Bull.* **2002**, 27, 705.
- (11) Meregallo, V.; Parrinello, M. *Appl. Phys. A* **2001**, 72, 143.
- (12) Darkrim, F.; Levesque, D. *J. Phys. Chem. B* **2000**, 104, 6773.
- (13) Ritschel, M.; Uhlemann, M.; Gutfleisch, O.; Leonhardt, A.; Graff, A.; Täschner, Ch. *Appl. Phys. Lett.* **2002**, 80, 2985.
- (14) Ruffieux, P.; Gröning, O.; Biemann, M.; Mauron, P.; Schlapbach, L.; Gröning, P. *Phys. Rev. B* **2002**, 66, 245416.
- (15) Lenardi, C.; Barborini, E.; Brioso, V.; Lucarelli, L.; Piseri, P.; Milani, P. *Diamond Relat. Mater.* **2001**, 10, 1195.
- (16) Donadio, D.; Colombo, L.; Milani, P.; Benedek, G. *Phys. Rev. Lett.* **1999**, 83, 776.
- (17) Barborini, E.; Piseri, P.; Li Bassi, A.; Ferrari, A. C.; Bottani, C. E.; Milani, P. *Chem. Phys. Lett.* **1999**, 300, 633.
- (18) Casari, C. S.; Li Bassi, A.; Bottani, C. E.; Barborini, E.; Piseri, P.; Podestà, A.; Milani, P. *Phys. Rev. B* **2001**, 64, 85417.
- (19) Hirscher, M.; Becher, M.; Haluska, M.; Quintel, A.; Choi, Y. M.; Dettlaff-Weglikowska, U.; Roth, S.; Stefanek, I.; Bernier, P.; Leonhardt, A.; Fink, J. *J. Alloys Compd.* **2002**, 330–332, 654.
- (20) Züttel, A.; Sudan, P.; Mauron, Ph.; Kyiobaiashi, T.; Emmenegger, Ch.; Schlapbach, L. *Int. J. Hydrogen Energy* **2002**, 27, 203.
- (21) Barborini, E.; Piseri, P.; Milani, P. *J. Phys. D: Appl. Phys.* **1999**, 32, L105.
- (22) Milani, P.; Piseri, P.; Barborini, E.; Podestà, A.; Lenardi, C. *J. Vac. Sci. Technol., A* **2001**, 19, 2025.
- (23) Gago, R.; Jiménez, I.; Albella, J. M. *Surf. Sci.* **2001**, 482–485, 530.
- (24) Stöhr, J. *NEXAFS Spectroscopy*; Springer: New York, 1992.
- (25) Hitchcock, A. P.; Mancini, D. C. *J. Electron Spectrosc.* **1994**, 67, 1.
- (26) *MATLAB*, v. 6.5; The Mathwork Inc.: Natick, MA, 2002.
- (27) Fallon, P. J.; Veerasamy, V. S.; Davis, C. A.; Robertson, J.; Amaratunga, G. A. J.; Milne, W. I.; Koshinen, J. *Phys. Rev. B* **1993**, 48, 4777.
- (28) Zoppi, L.; Colombo, L. *Eur. Phys. J. B* **2002**, 27, 355.
- (29) Darkrim, F.; Levesque, D. *J. Phys. Chem. B* **2000**, 104, 6773.
- (30) Hirschfelder, J. O. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
- (31) Volpe, M.; Cleri, F. *Chem. Phys. Lett.* **2003**, 371, 476.