Cluster-Beam Deposition and *in situ* Characterization of Carbyne-Rich Carbon Films

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Nanostructured carbon films produced by supersonic cluster beam deposition have been studied by *in situ* Raman spectroscopy. Raman spectra show the formation of a sp^2 solid with a very large fraction of sp-coordinated carbyne species with a long-term stability under ultrahigh vacuum. Distinct Raman contributions from polyyne and cumulene species have been observed, as well as different stabilities under gas exposure. Our experiments confirm theoretical predictions and demonstrate the possibility of producing a carbyne-rich pure carbon solid. The stability of the sp^2-sp network has important implications for astrophysics and for the production of novel carbon-based systems.

Linear carbon chains with sp hybridization are considered as fundamental constituents of the interstellar medium [1,2]. They are abundant in circumstellar shells [1] and their presence can account for many features of the diffuse interstellar bands [1,2]. The efforts to synthesize and study these species in laboratory has stimulated the discovery of C_{60} [3]. Several gas-phase studies of carbon clusters with linear or cyclic structure have suggested that they can be elemental building blocks of three-dimensional fullerenes and nanotubes [4].

The sp carbon chains can present alternating single and triple bonds (polyyne) or only double bonds (poly-cumulene) [5]. Theoretical calculations suggest that poly-cumulenes are less stable than polyynes [5,6]. Both species are characterized by an extremely high reactivity against oxygen and a strong tendency to interchain cross-linking [7], thus rendering the direct observation of a pure carbyne-assembled solid still a major challenge. Isolated carbynic species have been investigated in the gas phase in order to determine their geometry [4,8]; their electronic and vibrational structure has been studied for noninteracting clusters embedded in matrices of cold rare gases [9].

The sp carbon chains have also been proposed as the elemental building blocks of a carbon allotrope called carbyne [7]. The carbyne story is very controversial: The first claims of direct observation of carbyne date back from the 1960s [10,7]; however, until now, no firm and unambiguous evidence of the existence of this allotrope has been provided [7]. Experimental results, mainly based on crystallographic recognition supporting the identification of crystalline carbyne, have been the object of strong criticism up to a complete rejection of the carbyne concept [7,11].

Although the occurrence of crystalline carbyne is still a matter of debate, carbyne-rich or carbynoid solids have been produced by synthetic strategies mainly based on chemical routes. These include oxidative coupling reactions, dehydrohalogenation of polymers, polycondensation reactions of halides, electrochemical reductive carbonization, and condensation of end-capped chain molecules produced in the gas phase [12–15]. In these systems polyyne chains, assembled together, are preserved against cross-linking and chemical decomposition by the presence of metal-based species and molecular groups terminating and separating the chains.

A different approach to the synthesis of carbyne is the high temperatures and high-pressure treatment of carbon-based materials. Resistive heating of graphite, high-energy laser, or ion irradiation of carbon have been suggested as possible methods to produce carbynoid materials [16]. However, no definitive confirmation of the validity of these methods has been reported thus far.

Raman spectroscopy is one of the techniques of choice for the study of carbon-based materials and for the identification of carbyne [7,17]. The presence of a Raman band at roughly 2100 cm^{-1}, generated by the carbon triple bond, is admitted to be one of the strongest arguments in favor of the presence of carbynes [7,14]. Raman spectra of carbynoid materials are characterized by G and D bands in the 1200–1700 cm^{-1} range as in amorphous carbon and by the presence of the band in the 2100 cm^{-1} region [7,14]. For carbyne-rich materials, this band should have an intensity comparable or even greater than the amorphous contribution.

Raman spectra from chemically stabilized carbynoid systems are reported in literature; due to the high reactivity and fast aging of the carbyne species, no Raman spectra are reported for pure carbon systems.

In this Letter, we show that it is possible to produce nanostructured carbon films rich of carbyne species by depositing pure carbon clusters from a supersonic beam. We have characterized these films by *in situ* Raman spectroscopy determining the contribution to the spectra

coming from the polyyne and cumulene species. We have also studied the aging of the film and the effect of different gas exposure.

The deposition of carbon clusters was performed by means of an UHV cluster beam apparatus (CLARA, cluster assembling roaming apparatus) described in detail in [18]. Cluster beams are generated by a pulsed microplasma cluster source [19]. Cluster mass distribution is monitored prior to deposition by a reflectron time-of-flight mass spectrometer. Cluster mass distribution is peaked around 600 atoms per cluster and it extends up to several thousand atoms per cluster. Cluster kinetic energy is roughly 0.3 eV/atom so that the deposition occurs in the low-energy regime, in which negligible fragmentation of clusters takes place. In previous works, we have demonstrated that low-energy carbon cluster deposition allows the production of films having a structure at the nanoscale. This is due to the fact that cluster fragmentation is almost absent and, hence, carbon nanoparticles retain their individuality in the film [20,21].

In order to perform both the synthesis and the analysis of the films under UHV conditions, we have connected CLARA with a small chamber equipped with a substrate holder capable of three-axis translation and rotation around the vertical axis. Nanostructured carbon films with a thickness of 200 nm were grown on a silicon substrate at room temperature. After the deposition, the sample was positioned (by 90° rotation) in front of a fused quartz viewport. Raman measurements in backscattering geometry have been performed *in situ* with a Jobin-Yvon T64000 spectrometer, in triple grating configuration (1800 grooves/mm gratings) and with the 532 nm line of a frequency doubled Nd-Yag Coherent DPSS 532 laser. The detector was a liquid nitrogen cooled charge-coupled device camera. The instrument spectral resolution is below 3 cm^{-1}.

Cluster-assembled carbon films have been previously characterized *ex situ* by Raman spectroscopy [21]. The films have an amorphous structure with a main sp^2 hybridization character. The G and D features reveal a substantial amount of distortion of bond lengths and angles [22]. A weak peak at about 2100 cm^{-1} was observed. Because of the high reactivity of carbyne, this peak could be attributed to a residual presence of a primeval larger carbynoid population. However, a definitive attribution based solely on *ex situ* data cannot be considered as definitive.

Figure 1 shows the comparison between the *ex situ* and the *in situ* Raman spectra of two films deposited in the same conditions. G and D bands are almost identical, whereas the peak at 2100 cm^{-1} has dramatically increased in intensity in the *in situ* spectrum (we will refer to it as "C" peak). This peak has a remarkably strong intensity and appears to be structured and composed of a main broad peak at about 2100 cm^{-1} and a weaker shoulder centered around 1980 cm^{-1}, as evidenced by a
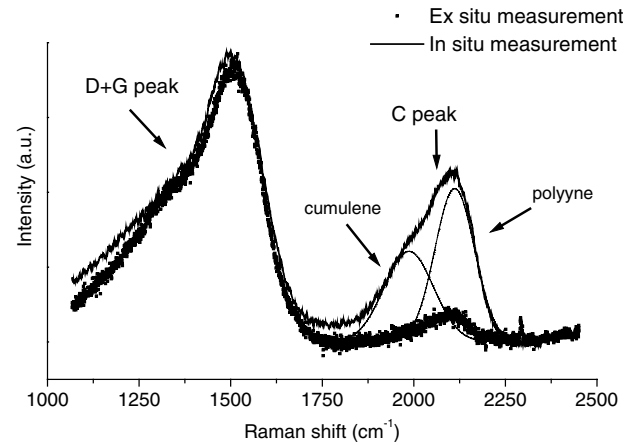

FIG. 1. Raman spectra of nanostructured carbon films deposited by a supersonic cluster beam, measured *ex situ* (dotted) and *in situ* in UHV conditions (continuous). For the second spectra, we have indicated the two fitting curves identifying the cumulene (left) and polyyne (right) contributions.

two-Gaussian fit (see Fig. 1). The relative C-peak intensity, expressed by the ratio between its integrated intensity and the *D-G* band integrated intensity ($I_C^{\text{rel}} = I_C/I_{D,G}$), is roughly 45%.

Raman spectra confirm the formation of a carbynoid material with a substantial presence of sp linear structures among a sp^2 hybridized disordered network, although it is not possible to quantify the amount of sp hybridized C atoms, since the Raman cross section of this kind of vibration is unknown. Compared to other carbynoid systems reported in literature [7], the C-peak at 2100 cm^{-1} presents a low-frequency shoulder at 1980 cm^{-1}. This is caused by the presence of both cumulenic and polyynic chains coexisting in the film and giving spectral contributions at different frequencies [23]. The broadening of the two components can be ascribed to the sp chain length distribution and to disorder [7]. These observations show that a carbyne-rich material can be formed by assembling carbon clusters at very low energies without high temperature and high-pressure or chemical reactions inducing carbyne formation from polymers or hydrocarbons. As previously reported in Ref. [18], we have performed *in situ* characterization of cluster-assembled films by electronic spectroscopy, confirming the absence of contaminants such as oxygen or nitrogen.

We have studied the carbynoid material stability through the evolution of the C-peak intensity, keeping the sample in UHV for several days (at a pressure of about 2×10^{-9} Torr) and collecting Raman spectra at fixed time intervals (Fig. 2). We observed a slow decrease of the intensity of both the two components of the C peak. Again no evident changes in the shape of G and D bands has been observed. This allows us to study the C-peak intensity evolution by means of the previously defined integrated intensity ratio I_C^{rel}. It is also reasonable to
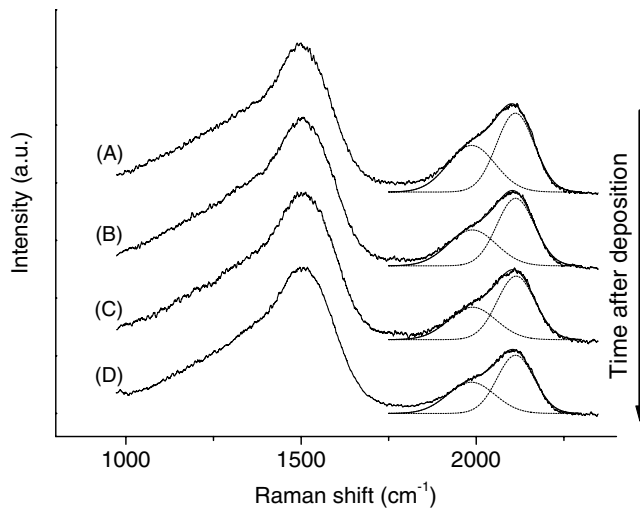
FIG. 2.   Raman spectra of a 200 nm thick sample kept in UHV at different times; immediately after the deposition (*A*) and after 18 h (*B*), 46 h (*C*), and 18 days (*D*). Gaussian fit of the two components of the carbyne peak is also reported.

assume a relationship between the intensity of the carbyne peaks and their concentration, even though it is not possible to make a quantitative evaluation.

The temporal evolution of I_C^{rel} is well described by an exponential decay plus a constant (Fig. 3). This provides an estimate of the characteristic decay time constant and of the residual nonreacted fraction of carbynes. The sample kept in UHV showed a characteristic decay time of the order of 22 h, resulting in a reduction of I_C^{rel} to a 29% of the sp^2 component. It is worth noting that this residual intensity is almost 1 order of magnitude greater than the intensity measured in *ex situ* samples, and that it remains stable even after 18 days from the deposition. In addition, the relative stability of *D* and *G* bands reveals that the amorphous structure is not significantly affected by the changes and rearrangements occurring to the carbynoid component.

This observation addresses a very important and unexpected point concerning carbyne stability: In our cluster-assembled films, polyyne and cumulene species survive the soft landing and are stabilized in a pure carbon environment. The carbyne interaction with other types of clusters is such that, after a spontaneous degradation, probably due to cross-linking, the amount of carbynoid species remains quantitatively very high and constant.

The introduction of dry air into the deposition chamber strongly modifies the Raman spectrum as shown in Fig. 4. As in the UHV experiment, we have collected several Raman spectra as a function of exposure time of the film to the gas. We observed a fast decrease of the C-peak intensity (see Fig. 3) with a decay time constant of 35 min and a residual intensity of 3.6%, comparable with that observed in *ex situ* measurements [21]. The two compo-
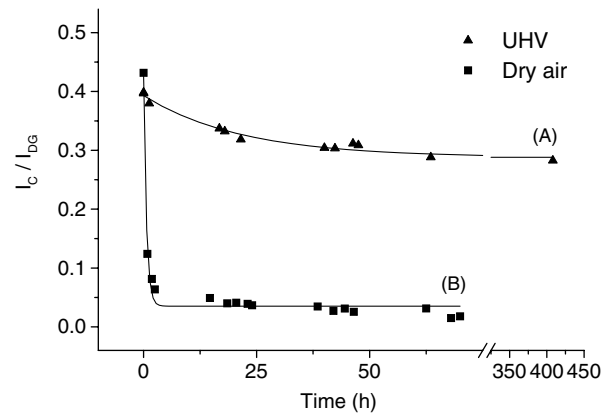

FIG. 3.   Decay behavior of the relative C peak intensity as a function of UHV residence (*A*) and dry air exposure time (*B*). The exponential plus constant fit of the experimental data is represented by the continuous line.

nents of the C peak behave differently under dry air exposure. After several decay times, a two-Gaussian fit shows the complete disappearance of the lower frequency peak generated by the cumulene fraction. This indicates a more pronounced stability of the polyyne configuration against oxygen exposure, confirming the theoretical predictions [7,23]. At the same time, we have observed a $20\ \text{cm}^{-1}$ blueshift of the position of the two peaks. According to Akagi *et al.* [24], the frequency of carbynic Raman peaks has an inverse dependence on the number of carbon atoms composing the chain. This behavior suggests the attribution of the observed blueshift to a decrease in the average chain length of the deposited carbynes. Remarkably, there was no clear evidence for a similar shift in UHV experiments.
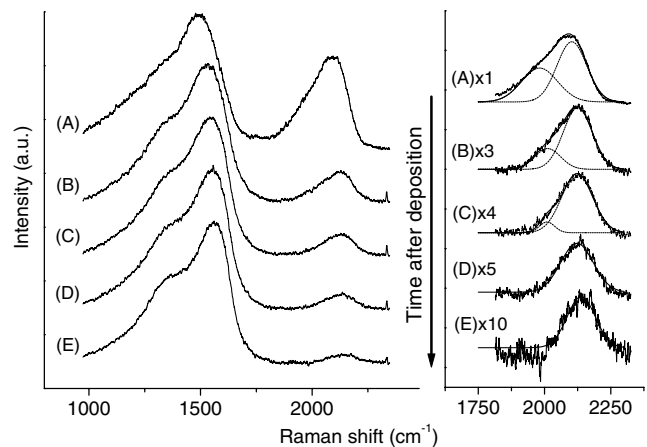

FIG. 4.   Left panel: Raman spectra of a 200 nm thick sample exposed to dry air at different times; immediately after the deposition (*A*) and after 50 min (*B*), 2.5 h (*B*), 15 h (*C*), and 70 h (*E*). Right panel: Evolution of the corresponding carbyne peak and Gaussian fit of its two components. The scale factor is also reported.

In order to further clarify the role of oxygen, we have repeated the measurements exposing a film to 500 mbar of pure nitrogen (N_2). We have observed an intermediate behavior for both the decay time and the residual intensity in comparison with the UHV and dry air behavior. A blueshift of about 10 cm^{-1} was also observed, but no disappearance of the cumulene peak took place.

The experimental results reported here provide new elements for the interpretation of the carbyne puzzle and are of relevance for areas where carbon clusters play an important role such as the composition of the interstellar medium and the existence of new allotropic forms of carbon. Low-energy cluster beam deposition in an oxygen-free environment appears to be a viable technique for the production of a pure carbon nanostructured material extremely rich of carbynoid species. The unexpected high stability of polyyne and cumulene species interacting with each other and with fullerene-like-type of clusters once deposited [20], suggests the existence of a cluster-cluster reaction mechanism leading to the formation of networks where the sp bondings are stabilized. These networks composed by sp^2 and sp linkages may be a disordered analogue of a new phase of carbon called graphyne and theoretically predicted by Baughman *et al.* [25]. The doping of this material with alkali metals or stabilizing molecular groups may lead to observation of novel structural and functional properties in these systems.

The gas-phase chemical models of interstellar clouds take into account the presence of different carbon nanoparticles such as carbyne, fullerenes, polycyclic aromatic hydrocarbons, etc. [1,26]. These species are related by very complex reaction pathways to produce and destroy one species from the others. Our observations suggest that cluster-cluster interaction can produce large carbonaceous grains where carbyne species are present and stable.

In conclusion, we have characterized by *in situ* Raman spectroscopy nanostructured carbon films produced by supersonic cluster beam deposition in UHV conditions. Raman spectra show the presence of a large quantity of polyyne and polycumulene moieties in the films, giving origin to peaks at 2100 and 1980 cm^{-1}, respectively. The carbyne species are substantially stable in an oxygen-free environment. We have characterized carbyne reactivity as a function of time in UHV and in the presence of dry air and nitrogen showing that oxygen almost completely destroys the carbyne fraction of the films. We have demonstrated that polycumulenes are less stable against oxygen compared to polyynes. The decay kinetics of the carbynoids exposed to gas gives information about the chemical and thermodynamical nature of the degradation processes. We have shown that sp carbon clusters can be assembled and stabilized at room temperature in a pure carbon environment allowing the spectroscopic characterization of a different type of bondings. Moreover, we have demonstrated the usefulness of *in situ* Raman spectroscopy for the study of nanostructured carbon. Our experiments open new perspectives for the production and the study of the long-sought sp carbon allotropes.

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[1] W. W. Duley, Astrophys. J. **528**, 841 (2000).

[2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Astrophys. J. **314**, 352 (1987).

[3] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[4] J. Hunter, J. Fye, and M. F. Jarrold, Science **260**, 784 (1993).

[5] R. B. Heimann, J. Kleiman, and N. M. Salansky, Nature (London) **306**, 164 (1983).

[6] M. J. Rice, S. R. Phillpot, A. R. Bishop, and D. K. Campbell, Phys. Rev. B **34**, 4139 (1986).

[7] For a review, see *Carbyne and Carbynoid Structures*, edited by R. B. Heimann, S. E. Evsyukov, and L. Kavan (Kluwer, Dordrecht, 1999).

[8] M. T. Bowers *et al.*, Science **260**, 1446 (1993).

[9] J. P. Maier, J. Phys. Chem. A **102**, 3462 (1998); J. Szczepanski *et al.*, Spectrochim. Acta, Part A **57**, 775 (2001).

[10] A. E. Goresy and G. T. Donnay, Science **161**, 363 (1968).

[11] A. G. Whittaker, Science **229**, 485 (1985); P. P. K. Smith and P. R. Buseck, *ibid.* **229**, 487 (1985).

[12] Yu. P. Kudryavtsev, R. B. Heimann, and S. E. Evsyukov, J. Mater. Sci. **31**, 5557 (1996).

[13] L. Kavan, Chem. Rev. **97**, 3061 (1997).

[14] J. Kastner *et al.*, Macromolecules **28**, 344 (1995); L. Kavan, *et al.*, Carbon **33**, 1321 (1995).

[15] R. J. Lagow *et al.*, Science **267**, 362 (1995).

[16] J. A. Lenz *et al.*, J. Appl. Phys. **89**, 8284 (2001).

[17] M. Nakamizo, R. Kammereck, and P. I. Walker, Jr., Carbon **12**, 259 (1974).

[18] E. Barborini *et al.*, Rev. Sci. Instrum. **73**, 2060 (2002).

[19] E. Barborini, P. Piseri, and P. Milani, J. Phys. D **32**, L105 (1999).

[20] D. Donadio *et al.*, Phys. Rev. Lett. **83**, 776 (1999).

[21] E. Barborini *et al.*, Chem. Phys. Lett. **300**, 633 (1999).

[22] J. Robertson, Prog. Solid State Chem. **21**, 199 (1991).

[23] J. Kürti *et al.*, Synth. Met. **71**, 1865 (1995).

[24] K. Akagi *et al.*, Synth. Met. **17**, 557 (1987).

[25] R. H. Baughman, H. Eckhardt, and M. Kertesz, J. Chem. Phys. **87**, 6687 (1987).

[26] R. P. A. Bettens and E. Herbst, Astrophys. J. **468**, 686 (1996).