Carbon 'fluffy' aggregates produced by helium - hydrocarbon high pressure plasmas as analogs to interstellar dust

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ABSTRACT
The present study provides an investigation on the deposition of carbon-related products on different substrates using a high power dielectric barrier discharge fed with helium and saturated hydrocarbon gases. The discharge has been characterized by means of voltage-current measurements, while the neutral species and the dissociation compounds accumulated in the plasma reactor have been analyzed by Fourier-transform infrared (FTIR) spectroscopy. The properties of non-aromatic hydrogenated amorphous carbon (a–C:H) films and 'fluffy' carbon dust deposited onto various substrates are analyzed by FTIR and X-ray photoelectron spectroscopy. The sp²-hybridized fraction of a–C:H films is negligible while for the 'fluffy' dust, does not exceed 10%. The microscopic appearance, the hierarchical organization and the CH₂/CH₃ ratio around 2 of the 'fluffy' dust analog are results that supports the current understanding of cosmic carbon dust physico-chemical properties.

Key words: plasmas – astrochemistry – (ISM:) dust, extinction – infrared: ISM – Galaxy: center

1 INTRODUCTION
Infrared emission and absorption spectroscopy or imaging, applied for the study of astronomical objects, revealed many insights into the organic chemistry in space. Many satellites, space telescopes, airborne telescopes or ground based telescopes, were designed to host scientific instruments dedicated to specific wavelength ranges in near, mid and far infrared. The upcoming mission of NASA, ESA and CSA, will carry the James Webb Space Telescope (JWST) on board and after the successful deployment of the infrared telescope, the scientific community will have access to new observational data, at high resolution and may shed some new light on the hypotheses concerning the carbon compounds and their processing in space. On one hand, the presence of infrared emission bands with central wavelengths ranging from 3 μm to 12 μm (i.e. the so-called unidentified infrared bands) and related to carbon based molecules was detected for many astronomical objects. More specific, bands observed at 3.3, 6.2, 7.7, 8.6 and 11.3 μm, where initially associated with aromatic carbon vibrational features and led to the construction of polycyclic aromatic hydrocarbon (PAH) hypothesis in 1985 (Leger & Puget 1984; Allamandola et al. 1985). On the other hand, infrared absorption spectroscopy data towards various lines of sight, Galactic or extragalactic, provided enough data to understand that, under astronomical conditions, no unique chemical composition exists for the carbon dust. Instead, carrier families based on hydrogenated amorphous carbon (HAC or a–C:H), a hypothesis launched back in 1983 (Duley & Williams 1983), are considered to be responsible for the observations of specific environments, such as Galactic center sources, dense clouds or diffuse interstellar medium. Usually, a mixture of aliphatic (e.g. 3.4, 6.9 and 7.3 μm) and aromatic absorption features are observed, the aromatic to aliphatic ratio being function on the local thermodynamic parameters, radiation fields and hydrogen content. In order to match the astronomical observations and to elucidate the source of the unidentified infrared bands, efforts have been made either to theoretically...
assesses the carbon materials molecular structure and spectral properties (Peeters et al. 2002; Gray & Edmunds 2004; Cohen & Barlow 2005; Li & Dra 2008; Dra 2008; Li & Dra 2012; Papoular 2013; Dhanou & Rawlings 2014; Mauney & Lazatti 2016) or to design experiments for appropriate Earth based synthesis of analog materials (Colangeli et al. 1997; Mennella et al. 2001a, 2002a; Rotundu et al. 2002; Kovačević et al. 2005; Stefanović et al. 2005; Dartois et al. 2007; Stefanović et al. 2007; Pino et al. 2008; Bennier et al. 2009; Carpentier et al. 2012; Gadallah et al. 2013).

In order to mimic the chemical and typological features of interplanetary and interstellar carbon dust, many synthesis methods have been proposed based on condensation experiments (Huisken et al. 2009; JAdger et al. 2009), physical vapor deposition (Dartois et al. 2005), combustion and pyrolysis methods (Colangeli et al. 1997; Pino et al. 2008; Bennier et al. 2009; Carpentier et al. 2012; Gadallah et al. 2013; Gavilan et al. 2016, 2017), pulsed laser deposition (Mennella et al. 2002b; JAdger et al. 2008; Godard et al. 2011; Gadallah et al. 2012, 2013) and plasma enhanced chemical vapor deposition (Colangeli et al. 1997; Kovačević et al. 2005; Stefanović et al. 2005, 2007; Maté et al. 2016; Molpeceres et al. 2017).

For a long time, the plasma processes were widely used for the assisted synthesis of carbon-based products, in various allotropic forms (e.g. amorphous carbon with controllable hydrogen content, graphite, diamonds, fullerences, graphenes, nanotubes etc.) and solid-state appearance (soot powders, thin films and thick films, coatings). Various recent technological solutions and process operational parameters can be employed in order to tune the properties of the carbon-based material and to obtain high purity products with optimized costs: the thermal vs nonthermal plasma process, electrical excitation methods, the composition of working gas, the plasma characteristic temperatures and the substrate temperature (Churilov et al. 1999; Dumay et al. 2002; Chen et al. 2003; Hatakeyama et al. 2003; Keidar et al. 2010; Agemi et al. 2011; Vizireanu et al. 2012; Kang et al. 2013; Levchenko et al. 2013; Sirghi et al. 2015; Ichimura et al. 2017; Vizireanu et al. 2017).

In this respect, the plasma based synthesis became a widespread solution to obtain carbon dust and particles (Shoji et al. 2006; Nagai et al. 2008; Ohno et al. 2009; Pristavita et al. 2011; Al Makdessi et al. 2017; Assens et al. 2017) or carbon interstellar dust analogs, mainly as thin films deposited onto various substrates (Kovačević et al. 2005; Stefanović et al. 2007; Gadallah et al. 2013; Molpeceres et al. 2017). Moreover, the plasma synthesized dust analogs can be used in laboratory studies concerning the effects of different physical agents on structural properties, in order to mimic astrophysical processes or observed spectral features. For example, the exposure of hydrogenated amorphous carbon samples to 160 nm UV photons, at doses comparable with the average doses in the diffuse interstellar medium, was carried out in order to obtain information on spectroscopic features of dust in diffuse interstellar medium such as the UV bump at 217 nm (4.6 μm⁻¹) (Gadallah et al. 2011; Gavilan et al. 2016) or the mid-far infrared bands (Mennella et al. 2001b; Gadallah et al. 2012; Maté et al. 2014; Gavilan et al. 2017). Moreover, exposure of hydrogenated amorphous carbon samples to an electron beam of 5 keV energy, was found to be an approach in studying the decay of the 3.4 μm band, characteristic to destruction of CH₃ and CH₂ groups in dense clouds by cosmic rays (Maté et al. 2014, 2016). Other works were focused on ion irradiation of analogs, aiming to find explanations for the aliphatic C–H bonds destruction by cosmic rays (Godard et al. 2011; Dartois et al. 2017).

Among the plasma assisted synthesis methods, the plasma generated using the dielectric barrier discharge (DBD) is not commonly used for carbon particles deposition, although the DBD technique is widely used for long time in surface treatment (Boria et al. 2003; Liu et al. 2004; Boria et al. 2006; De Geyer et al. 2007; Morent et al. 2008; Asandulesa et al. 2010a), plasma polymerization (Donohoe & Wydeven 1979; Klages et al. 2000; Fanelli et al. 2005; Girard-Lauriault et al. 2005; Asandulesa et al. 2010b; Merche et al. 2012; Asandulesa et al. 2013), nanocomposite thin films deposition (Jidenko et al. 2007; Caquineau et al. 2009; Vallade et al. 2014; Bazinette et al. 2016; Brunet et al. 2017, 2018), gas conversion (Eliasson et al. 2000; Liu et al. 2001; Chiper et al. 2010; Obradović et al. 2011; Schiorlin et al. 2016), decontamination, sterilization or inactivation (Heise et al. 2004; Eto et al. 2008; Chiper et al. 2011; Daeschlein et al. 2012; Cullen et al. 2018) and life science applications (Kuchenbecker et al. 2009; Rajasekaran et al. 2009; Brehmer et al. 2015; Rezaei et al. 2016; Ito et al. 2018). Nevertheless, some specific studies employing DBD, were performed in connection with space science (Wang et al. 2008; Thejaswini et al. 2011; Mihaila et al. 2016). Overall, the DBDs have attracted a significant research interest due to the flexibility to fit into more complex plasma diagnostics set-ups, their relatively standardized electrical excitation methods, their operation at atmospheric or sub-atmospheric pressure, the absence of ion etching processes, high collisionality and low Debye length, low ionization degree and low gas temperature, the pulsed chemistry and the relatively high amount of reactive species generated per unit volume.

In this work, we present a new laboratory-scale method to synthesize carbon dust analogs using the sub-atmospheric pressure plasma generated in DBD reactor fed with helium in mixture with several hydrocarbon gases (i.e. CnH2n+2, with n = 1–4). The plasma assisted hydrocarbon gas conversion was successfully proved by means of gas infrared spectroscopy, either into lower mass hydrocarbons, with the same general formula or new compounds, such as C₃H₂ or C₂H₄. This is a new low temperature synthesis method for carbon dust analogs in form of both, films and dust products, no other experimental observations being available using a similar plasma device. Furthermore, we discuss the properties of hydrogenated amorphous carbon films and the 'fluffy' carbon dust, deposited onto various substrates, from a chemical and morphological point of view.

2 Experimental Details
2.1 Dielectric barrier discharge reactor

The carbon interstellar dust analogs were deposited on various substrates using a plasma assisted process, based on high power impulse DBD reactor, hosted by a stainless steel chamber shown schematically in Fig. 1, able to generate helium-hydrocarbons plasmas at sub-atmospheric pressure (80 kPa). Prior to each deposition, proper measures
were taken in order to reduce impurity contamination, i.e. atmospheric nitrogen, oxygen, carbon dioxide and water molecules adsorbed on the reactor walls. The stainless steel chamber was periodically pumped down to residual pressure of 2.6 Pa and heated up to 70 °C for several hours to allow an appropriate thermal desorption process.

The plasma is generated in a DBD assembly, fixed horizontally, composed out of two identical Aluminum electrodes (area of 43 cm²), taped on glass dielectric plates (1 mm thickness) and separated by a 5 mm gas gap. The bottom electrode was grounded and the top electrode (i.e. the power electrode) was connected to the output of a nanosecond high voltage pulses circuit, composed of a fast transistor high voltage switch (Belhik HTS 301), backed by a DC high voltage power supply (Glassman High Voltage series KL) and triggered by a Wave Function Generator (Tektronix AFG 3022C or AF 3022B). Positive high voltage pulses of about 6 kV amplitude, 1 kHz frequency and 500 ns duration were applied on the power electrode, producing an electric field large enough to breakdown the helium-hydrocarbon gas mixture, generating an electrical discharge, confined inside the inter electrode gap. A type-K thermocouple is fixed in the middle of the inter electrode gap and its output is connected to a laboratory multimeter (UNI-T UT 71C), with the data logging optical USB communication interface enabled. The light emission from the discharge was analyzed using an Triax 550 scanning monochromator spectrometer equipped with a CCD detector (Symphony Jobin Yvon Inc.).

Various types of substrates, such as flexible graphite (GoodFellow Co.), silicon, quartz and NaCl plates with approximately 1 cm² in surface area, were placed directly onto the ground electrode. Gas lines are connected to the DBD reactor and the gas flow is regulated by electronic mass flow controllers (Alicat Scientific, MC Series): helium (99.996%) and the precursor hydrocarbon gases (methane - CH₄, ethane - C₂H₆, propane - C₃H₈, butane - C₄H₁₀, 99.5%). The impurities level (ppm) for helium is H₂O < 5, O₂ < 5, while for hydrocarbon gases is O₂ < 100, N₂ < 600, H₂ < 500, other CₙHₘ < 3000, as stated by the producer, Linde Gas.

The DBD reactor was filled up with the gas mixture of He (85%) - CₙH₂n₊₂ (15%), at an initial total pressure of 80 kPa, then the reactor was sealed, the gas flow shut off and the plasma was ignited for 6 hours. The applied voltage and the ground line current were sampled using a high-voltage probe (Tektronix P6015A, 1000:1, 75 MHz) and a current probe (Pearson 6465, 1 V A⁻¹, 1.5 ns rise time; 200 MHz high frequency), monitored or periodically recorded using a digital oscilloscope (Tektronix TDS 5034B, 350 MHz, 5 GSa s⁻¹).

Infrared spectroscopy was selected to obtain information about the neutral species existing in the DBD reactor. Gas samples were obtained before and after the 6 hours plasma operation, using a vacuumed infrared gas cell with NaCl windows, connected to the reactor chamber. Transmission spectra in the range of 3600 – 700 cm⁻¹, with 1 cm⁻¹ spectral resolution, were recorded using a Bomem MB-104 Fourier transform infrared (FTIR) spectrometer.

2.2 Characterization of carbon-based materials

Two different types of hydrogenated carbon products are obtained in this study, as function of nucleation and growth processes on all substrates simultaneously present in the plasma during a single deposition step. On silicon, quartz and NaCl plates we obtain hydrogenated amorphous carbon thin films, while on flexible graphite 'fluffy' carbon dust particles are deposited. No DBD plasma sputtering was observed for all substrates used in our experiments and no deposition was observed if the hydrocarbon gases are absent from the gas mixture (i.e. if we use pure helium plasma or a gas mixture of helium (85 %) with hydrogen (15 %)). Taking this into account, different analysis techniques were chosen as function of the obtained carbon based product. The chemical characterization of the 'fluffy' carbon dust was carried out by means of scanning electron microscopy (SEM), diffuse reflectance ultraviolet-visible (UV-Vis) spectroscopy, FTIR spectroscopy and X-ray photoelectron spectroscopy (XPS).

Regarding the a-C:H thin films on NaCl, quartz and silicon substrates, the following analysis techniques were used: ellipsometry, FTIR, UV-Vis spectroscopy and XPS. The FTIR spectra of carbon based films deposited on NaCl substrates were recorded in transmittance mode (with 4 cm⁻¹ spectral resolution) using Bomem MB-Series 104 spectrometer. The 'fluffy' carbon dust deposited on flexible graphite was collected and analyzed by attenuated total reflectance (ATR) technique. Due to high refractive index of carbobaceous materials, a germanium crystal was mounted on a high Signal-to-Noise-Ratio spectrometer (Jasco FT/IR-4700 with ATR-Pro One accessory). For the FTIR transmission film measurement, the infrared beam diameter at the sample position is 15 mm while for ATR measurements, a 1.5 mm diameter germanium crystal mount was used. All recorded spectra were auto-baseline corrected with a second-order polynomial function and a scale brake was introduced to exclude residual CO₂ contribution from the spectrometer purge system.
The refractive indexes of a-C:H thin films were measured by principal angle-of-incidence ellipsometry technique using the reflection ellipsometer EL X-01R (632.8 nm HeNe laser). UV-Vis spectra of a-C:H thin films deposited onto quartz substrates were recorded using a dual beam spectrometer (Thermo Scientific Evolution 300) at 1 nm resolution. The diffuse reflectance UV-Vis spectra of obtained 'fluffy' carbon dust was measured with an integrating sphere (Avantes AvaSphere-50).

SEM observations have been made using the Quanta FEI 450 scanning electron microscope, operating at 30 kV applied on the electron gun. In order to prevent morphological change on the 'fluffy' carbon samples, the samples were not metal coated.

The XPS spectra of carbon-based materials deposited on silicon and flexible graphite substrates were recorded with a PHI 5000 VersaProbe (PHysical Electronics) spectrometer, using a monochromatic Al Kα X-ray source (1.486 keV), under a vacuum of about 2 × 10⁻⁶ Pa at a photoelectron take off angle of 45°. Regarding the spectra acquisition, the sputtering argon ion beam was not used in order to preserve the samples morphology.

3 RESULTS AND DISCUSSIONS

The main task of our study was to develop a new synthesis method, using atmospheric pressure plasmas, able to deposit carbon dust at low temperature, as analogs of the interstellar carbon grains, observed towards the galactic center or specific extragalactic objects. This section is dedicated to the comprehensive characterisation of both, the plasma phase and the deposition products.

3.1 Helium - hydrocarbon DBD plasmas

Due to fast rise and fall time (less than 50 ns) of the high voltage pulses and the large area of DBD electrodes, the current peak (Fig. 2) reaches 8 A for both, positive and negative current peaks, which corresponds to primary and secondary phases of the DBD discharges. Only slight variations of the current peaks were observed when the hydrocarbon gas type was changed. It should be pointed out here that the current, measured by the current probe, is the total current in the circuit. Mathematically, it represents the sum of the displacement current, corresponding to change oscillations inside dielectrics, the gas-gap capacitor or stray capacitors, and the conduction current, i.e. the actual discharge current. The maximum current density attains values of about 180 mA cm⁻². Keeping constant the voltage pulse amplitude at 6 kV and replacing the methane with higher molecular mass hydrocarbons, a slight decrease of the current peak, from 8 A to 6 A, was observed. This is due to supplementary energy consumption on additional molecular fragmentation by electron collisions. A shift of the current peak position was also observed for both, positive and negative current peaks. During the 6 hours of total plasma operation time, an increase of the peak values was noticed for the measured current, of around 20% over the initial value.

The analysis of the plasma emission spectra, reveals the presence of helium lines (388.8 nm, 501.6 nm, 587.6 nm, 667.8 nm, 706.5 nm, 728.1 nm), hydrogen alpha line (656.2 nm), as well carbon based radicals, the methylidyne (CH, band at 430 nm) and the diatomic carbon (C₂, band at 512 nm). The gas temperature, sensed by the thermocouple increased from room temperature, at the beginning of the experiments, to a maximum value of 35 °C after approximately 100 min and then remained constant till the end of plasma operation time.

The FTIR spectra of He/C₅H₂n+2 gas mixture obtained after plasma operation exhibits additional bands in comparison to spectra of the starting gas mixtures (Fig. 3). Prominent bands assigned to acetylene, centered at 3284 and 729 cm⁻¹, and ethylene characteristic bands centered at 1443 and 949 cm⁻¹ (Oleké & Störi 1991; Deschenaux et al. 1999; Linstrom et al. 2018) were observed. The bands located at 3085 and 1305 cm⁻¹ confirm the production of methane in the case of ethane, propane and butane containing plasmas as well. Also, we note the low level of carbon monoxide (2147 cm⁻¹) and the absence of carbon dioxide despite its usual strong absorption band in the infrared spectral region.

Different alkanes were utilized as precursor gases due to the fact that the main building blocks of plasma polymerization from volume fragments are sp²-hybridized CH₂ and CH₃ functional groups. During the gas conversion, new stable precursors form in small quantities (ethylene and acetylene) meaning that some sp³ and sp-hybridized groups may contribute to the plasma deposition process.

3.2 Hydrogenated amorphous carbon films

The obtained plasma polymerized hydrogenated amorphous carbon (a-C:H) thin films present different thicknesses as function of the precursor gas, for an identical deposition time. The thickness increases from hundreds of nanometers to micrometers with different deposition rates varying from nearly 1 (for methane) to 3.5 nm min⁻¹ (for butane). Compared to other studies involving AC voltage with high frequency DBD ethylene plasma (Fanelli et al. 2005), the deposition rates for our alkane plasmas are ten times smaller. Using acetylene as gas feed precursor, Mori et al. (2016) observed that the hydrogenated amorphous carbon poly-
Figure 3. FTIR spectra of the He/C_nH_{2n+2} gas mixtures, sampled before and after 6 hours of DBD plasma processing.

mer (a-C:H) synthesized by a dielectric barrier discharge-based plasma under atmospheric pressure can be composed by micro-structured particles. The growth of the particles can be controlled by gas dilution. The a-C:H film synthesized from C_2H_2/N_2 showed cauliflower-like particles, while the film synthesized from C_2H_2/He was composed of domed particles. Therefore, it is reasonable to assume that the deposition of (a-C:H) films is governed by an interplay of gas phase reactions and surface processes.

The a-C:H thin films deposited on NaCl, quartz and silicon substrates are transparent and colorless in the visible range (Fig. 4a). In the UV region absorption occurs at 250 nm (4.9 eV) related to π bonding of carbon atoms in sp^2 hybridization and at 217 nm (5.7 eV) due to sp^3 -σ-σ* transition (Logothetidis 2003; Dartois et al. 2005). Studies on optical and mechanical properties of amorphous hydrogenated carbon films (Gielen et al. 1996; Logothetidis 2003; Dartois et al. 2005) indicate that refractive index, elasticity, hardness depends on hydrogen content and sp^2 / sp^3 ratio. More recently, from a theoretical point of view Jones (2012a,b,c) shows that for a-C:H aliphatic materials, the CH_2 / CH_3 abundance ratio is correlated with hydrogen content that ranges in fixed limits. For our a-C:H films, plasma polymerized on NaCl and quartz substrates, the refractive index has an average of 1.4 emphasizing the soft, polymer-like, character of the films, with high value of hydrogen content, and the negligible sp^3 fraction. This is consistent with previous results by Dartois et al. (2005) which observed for high aliphatic and low olefinic or aromatic networks a value of the refractive index of 1.35.

The a-C:H films obtained in DBD plasma using different feed gases were analyzed by infrared spectroscopy (Fig. 4b). Specific to polymer-like amorphous carbon, common absorption bands of sp^3-hybridized carbon can be identified as: between 3000 and 2800 cm^{-1} (3.4 µm) due to aliphatic -C-H stretching, 1460 cm^{-1} (6.85 µm) –CH_2– scissor mode and 1375 cm^{-1} (7.25 µm) –CH_3 bending mode. Small absorption peaks of carbon sp^2-hybridized are found: 3080 cm^{-1} (3.3 µm) due to olefinic -σ=C–H asymmetric stretching and 1640 cm^{-1} (6.1 µm) due to olefinic -σ=C=C stretching. Absorption bands specific to oxygen bonds as 1700 cm^{-1} (5.9 µm) C=O (carbonyl group) stretching or the broadband from 3300 cm^{-1} (3 µm) O–H (hydroxyl group) stretching are insignificant, indicating a low level of oxygen contained in our a-C:H films. Similar to other results (Fanelli et al. 2005; Buijnsters et al. 2009) in our DBD synthesized a-C:H films, hydrogen is preferentially bonded to sp^3-hybridized C atoms.

The aliphatic sp^3 asymmetric modes ratio CH_2 group (2925 cm^{-1}) / CH_3 group (2955 cm^{-1}) give structural information about polymerized a-C:H films. Each bonding type has a different intrinsic strength (in units of cm group^{-1}) and these proportionality constants were used in previous similar analyses to calculate the column density of CH_2 and CH_3, as well the CH_2 / CH_3 ratio for various astronomical objects and analogs (Sandford et al. 1991; Pendleton et al. 1994; Jacob & Unger 1996; Ristein et al. 1998; Dartois et al. 2004, 2005; Chiari et al. 2013).

For 3.4 µm infrared band, the absorption strengths were evaluated using proportionality constant for CH_2 and CH_3 modes and the equation 1 from Chiar et al. (2013) arising

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**Wavelength (µm)**

| Wavelength (µm) | Methane (CH_4) |
|----------------|----------------|
| 2.8            | initial gas mixture |
| 2.9            | after 6 hours of plasma operation |
| 3.1            | initial gas mixture |
| 3.2            | initial gas mixture |
| 3.3            | initial gas mixture |
| 3.4            | initial gas mixture |
| 3.5            | initial gas mixture |
| 3.6            | initial gas mixture |
| 3.7            | initial gas mixture |
| 3.8            | initial gas mixture |
| 3.9            | initial gas mixture |
| 4.0            | initial gas mixture |
| 4.1            | initial gas mixture |
| 4.2            | initial gas mixture |
| 4.3            | initial gas mixture |
| 4.4            | initial gas mixture |
| 4.5            | initial gas mixture |
| 4.6            | initial gas mixture |
| 4.7            | initial gas mixture |
| 4.8            | initial gas mixture |
| 4.9            | initial gas mixture |
| 5.0            | initial gas mixture |
| 5.1            | initial gas mixture |
| 5.2            | initial gas mixture |
| 5.3            | initial gas mixture |
| 5.4            | initial gas mixture |
| 5.5            | initial gas mixture |
| 5.6            | initial gas mixture |
| 5.7            | initial gas mixture |
| 5.8            | initial gas mixture |
| 5.9            | initial gas mixture |
| 6.0            | initial gas mixture |
| 6.1            | initial gas mixture |
| 6.2            | initial gas mixture |
| 6.3            | initial gas mixture |
| 6.4            | initial gas mixture |
| 6.5            | initial gas mixture |
| 6.6            | initial gas mixture |
| 6.7            | initial gas mixture |
| 6.8            | initial gas mixture |
| 6.9            | initial gas mixture |
| 7.0            | initial gas mixture |
| 7.1            | initial gas mixture |
| 7.2            | initial gas mixture |
| 7.3            | initial gas mixture |
| 7.4            | initial gas mixture |
| 7.5            | initial gas mixture |
| 7.6            | initial gas mixture |
| 7.7            | initial gas mixture |
| 7.8            | initial gas mixture |
| 7.9            | initial gas mixture |
| 8.0            | initial gas mixture |
| 8.1            | initial gas mixture |
| 8.2            | initial gas mixture |
| 8.3            | initial gas mixture |
| 8.4            | initial gas mixture |
| 8.5            | initial gas mixture |
| 8.6            | initial gas mixture |
| 8.7            | initial gas mixture |
| 8.8            | initial gas mixture |
| 8.9            | initial gas mixture |
| 9.0            | initial gas mixture |
| 9.1            | initial gas mixture |
| 9.2            | initial gas mixture |
| 9.3            | initial gas mixture |
| 9.4            | initial gas mixture |
| 9.5            | initial gas mixture |
| 9.6            | initial gas mixture |
| 9.7            | initial gas mixture |
| 9.8            | initial gas mixture |
| 9.9            | initial gas mixture |
| 10.0           | initial gas mixture |
| 10.1           | initial gas mixture |
| 10.2           | initial gas mixture |
| 10.3           | initial gas mixture |
| 10.4           | initial gas mixture |
| 10.5           | initial gas mixture |
| 10.6           | initial gas mixture |
| 10.7           | initial gas mixture |
| 10.8           | initial gas mixture |
| 10.9           | initial gas mixture |
| 11.0           | initial gas mixture |

**Transmittance (a.u.)**

| Wavelength (nm) | Methane (CH_4) |
|-----------------|----------------|
| 2400            | initial gas mixture |
| 2500            | initial gas mixture |
| 2600            | initial gas mixture |
| 2700            | initial gas mixture |
| 2800            | initial gas mixture |
| 2900            | initial gas mixture |
| 3000            | initial gas mixture |
| 3100            | initial gas mixture |
| 3200            | initial gas mixture |
| 3300            | initial gas mixture |
| 3400            | initial gas mixture |
| 3500            | initial gas mixture |
| 3600            | initial gas mixture |

**Figure 3. FTIR spectra of the He/C_nH_{2n+2} gas mixtures, sampled before and after 6 hours of DBD plasma processing.**
C:H film structure is similar to polypropylene, but presents long aliphatic (alkane) chains H₃C−(CH₂)ₙ− with n greater than 4 (Buijsters et al. 2009; Gadallah 2015) and no aromatic C−H or C=C infrared signatures were found.

3.3 'Fluffy' carbon dust

In contrast with smooth and totally transparent films plasma polymerized on NaCl, quartz and silicon substrates, a 'fluffy' ash-like powder is formed on flexible graphite substrate. The deposition process is strongly influenced by the substrate nature, i.e. nucleation process on a graphite substrate appears to favor the synthesis of the 'fluffy' aggregates of dust carbon-based material. Optical microscopy and SEM studies of all samples, performed in different substrate regions and at various magnifications, covering the mesoscale range, show various morphological features of the 'fluffy' deposits (Fig. 5). An incomplete substrate coverage was observed for all studied conditions, the coverage degree being random for different samples, but higher than 50% in most cases (Fig. 5a). The carbon-based material synthesized onto flexible graphite is composed of inhomogeneous clusters, that are due to aggregation of individual flakes with characteristic dimensions down to nano-scale (Fig. 5b). A cauliflower-like growth is likely to take place during 'fluffy' dust carbon-based material deposition, explaining the microscopic voids visible at mesoscale (Zani et al. 2013) and the large internal surface area.

The largely inhomogeneous structures observed in SEM images, at different magnifications, for 'fluffy' carbon dust deposited onto flexible graphite substrates, indicates that the contribution of plasma volume reactions is insignificant and the formation of active sites that initiate and sustain the plasma polymer growth occurs at the substrate surface. This is typical to deposition process in DBD reactors, due to relatively high operating pressure and the subsequent very short mean free path.

The diffuse reflectance spectra of obtained 'fluffy' carbon dust (reflectance less than 5%) shows high absorption coefficient in the ultraviolet-visible-near infrared spectral range, with no significant photoluminescence effect. This result is consistent with those of Godard et al. (2011), that observed an absorption continuum due to electronic transitions for soot samples.

The refractive index for 'fluffy' carbon dust was estimated, from the theoretical studies of Jones (2012b,c) on physical properties of carbonaceous materials, to be around 2.

A typical FTIR-ATR spectrum of the 'fluffy' carbon dust deposited on flexible graphite in DBD plasma is shown in Fig. 6. The product was collected from the flexible graphite, placed on the germanium ATR crystal, covering the entire area. Using the ATR clamp screw, the dust was carefully pressed, ensuring a sample thicker than the penetration depth of the evanescent wave at infrared wavelengths. Due to the 'fluffy' appearance of the carbon dust, after the pressing process, air inclusions trapped in contact with the ATR crystal may still be present and diminish the absorption, resulting in a slight decrease of the optical depth values. The spectra reveals common and additional
absorption bands to a–C:H films of carbon sp\(^3\)-hybridized as: between 3000 and 2800 cm\(^{-1}\) (3.4 μm) due to aliphatic –C=H stretching, 1460 cm\(^{-1}\) (8.5 μm) –CH\(_2\) – scissor mode and 1375 cm\(^{-1}\) (7.25 μm) –CH\(_3\) bending mode. Based on the absence of the O–H hydroxyl group IR signature, the aliphatic ether C–O–C functional group has been identified at 1150 cm\(^{-1}\) (8.57 μm). Another ether functional group was identified at 1050 cm\(^{-1}\) (9.52 μm) most probably the methoxy R–O–CH\(_3\) due to plasma hydrocarbon working gases. Absorption bands of carbon sp\(^2\)-hybridized are found: 1700 cm\(^{-1}\) (5.9 μm) carbonyl C=O stretching and 1640 cm\(^{-1}\) (6.1 μm) specific to olefinic –C=C stretching. The olefinic =C–H asymmetric stretching at 3080 cm\(^{-1}\) (3.3 μm) is significantly small. Different types of alkene were identified in the fingerprint region as out of plane wagging modes of trans-alkene –CH=CH– at 965 cm\(^{-1}\) (10.36 μm) and vinylidene >CH=CH\(_2\) at 890 cm\(^{-1}\) (11.23 μm) (Dartois et al. 2005; Godard & Dartois 2010). No aromatic bands at 3050 cm\(^{-1}\) (3.28 μm) due to =C–H stretching or 1590 cm\(^{-1}\) (6.28 μm) due to –C=C stretching were found. The broad peak from 1500 cm\(^{-1}\) (6.66 μm) corresponds to residual water vapours from FTIR spectrometer chamber and have nothing in common with the fluffy dust.

The CH\(_2\) / CH\(_3\) ratio of 'fluffy' carbon dust is approximately 2, using the same calculation method as in the case of our DBD a–C:H film. This is similar to the average CH\(_2\) / CH\(_3\) ratio estimated for astronomical objects in diffuse interstellar medium (Sandford et al. 1991; Pendleton et al. 1994; Dartois et al. 2004, 2005, 2007).

Switching to different hydrocarbon plasma type, chemical composition analyzed by XPS of both hydrogenated amorphous carbon (a–C:H) polymer films and 'fluffy' carbon dust show similar results. The survey spectra shows dominant C1s peak while O1s and N1s are within detection limits (Fig. 7a). In all experimental conditions, the carbon-based films and also the 'fluffy' dust are not contaminated by N and O, as the C, N, O content is dominated by C at the 97% level, whereas O can contribute to at most 2% and N < 1%. No significant variations of relative atomic percent- age as function of hydrocarbon gas type was observed during this study. The presence of oxygen indicates that the surface of dust samples is slightly oxidized (either during synthesis, either due to ambient air exposure after deposition).

High resolution XPS spectra measured on a–C:H film deposited on silicon substrate and 'fluffy' carbon dust de-posited on flexible graphite as substrate, both synthesized in propane containing plasma were selected as example of carbon hybridization analysis. The C1s envelopes were deconvoluted using Grams Galactic software with 90% Gaussian - 10% Lorentzian peak fitting mixed profile (Fig. 7b). The Doniach-Sunjic asymmetric fitting function (Jackson 1995; Cunge et al. 2015) was excluded from our XPS fitting procedure due to non aromatic or non graphene-like character of our a–C:H film and 'fluffy' dust. As an example of asymmetric dependency, the XPS spectrum of flexible graphite was
Figure 7. XPS survey spectra (a) and high-resolution scan spectra over: a–C:H film deposited on silicon substrate and ‘fluffy’ dust deposited on flexible graphite in a propane containing plasma (b). 

overlapped on Fig. 7 for comparison. The accepted binding energy for C1s peak in pure graphite is 284.2 eV (± 0.2 eV) (Weckhuysen et al. 1998; Tien et al. 2011; Gaddam & Vander Wal 2013) with a full width at half maximum (FWHM) less than 1 eV (Filik et al. 2003) and a satellite peak shifted with ∼ 6 eV to higher binding energy, specific to π–π* ring transition (Jackson 1995; Asandulesa et al. 2013; Gaddam & Vander Wal 2013).  

The main contribution to C1s envelopes for both, a–C:H film and ‘fluffy’ dust (Fig. 7b) was assigned to saturated aliphatic hydrocarbon sp3 hybridized, carbon atoms from C–C bonds and CH2 or CH3 functional groups at the binding energy of of 285.1 eV (± 0.2 eV) (Weckhuysen et al. 1998; Tien et al. 2011; Gaddam & Vander Wal 2013). For high concentrations of sp3 hybridized C atoms, the C1s peak tend to gain in shape symmetry and is slightly shifted towards higher binding energy in respect with sp2 carbon derived from a standard graphite. Chemical shifts of +1.5 eV and +3 eV are typically assigned to aliphatic ether C–O–C and carbonyl C=O functional groups (Weckhuysen et al. 1998; Tien et al. 2011; Gaddam & Vander Wal 2013; Varga et al. 2017). Small amount of hydrogenated aliphatic carbon, sp2 hybridized was assigned to olefinic C=C bonds, as also probed by infrared analysis, at a chemical shift of −1.1 eV from the main sp3 hybridized carbon peak (Weckhuysen et al. 1998; Artemenko et al. 2015; Varga et al. 2017).  

The sp2 satellite peak specific to π–π* ring transition, is not present in main C1s peak of both, a–C:H film and ‘fluffy’ dust, revealing no aromatic ring in a–C:H film and ‘fluffy’ dust backbone. 

XPS survey (Fig. 7a) shows a low level of oxygen and nitrogen contamination. Typical infrared signatures of amine, carboxyl and hydroxyl groups are below the detection limit of the infrared spectrometer and from this point of view their contribution to C1s envelope of a–C:H film and ‘fluffy’ dust was neglected. Nevertheless, taking into account the surface contamination processes and knowing that typical depth probed by XPS is less than 5 nm, the ether C–O–C and carbonyl C=O components area might include small contribution from C–N and O–C=O functional groups. 

By combining all potential sp3 and sp2 hybridized in aliphatic carbon bonding type described by XPS analysis, the sp2 fraction for a–C:H films is negligible. In the case of the ‘fluffy’ dust, the sp2 fraction does not exceed 10%. These results are also confirmed by the infrared analysis. 

4 ASTROPHYSICAL IMPLICATION AND CONCLUSIONS

The laboratory production of carbonaceous compounds as analogs to interstellar dust extends now over many decades and it was always of great help for astronomers concerning the composition of the interstellar dust grains. Using multiple analysis techniques, we have shown in this paper that the high power impulse dielectric barrier discharge in helium and hydrocarbon gas mixtures, is a suitable method for laboratory synthesis of ‘fluffy’ aggregates, as analogs to interstellar dust grains, exhibiting both chemical and morphological similarities. 

Regarding the composition of interstellar carbon dust, infrared observations of localized sources (Sandford et al. 1991; Pendleton et al. 1994) or along the line of sight toward Sgr A* (Chiar et al. 2000), IRAS 08572+3915 (Dartois et al. 2007), IRAS 19254-7245 (Risaliti et al. 2003), NGC 1068 (Marco & Brooks 2003) and NGC 5506 (Imanishi 2000), confirm the presence of a solid hydrogenated carbon based material with aliphatic character identified by infrared absorption centered at 3.4, 6.85, and 7.25 µm. The FTIR spectra of both, the a–C:H films and ‘fluffy’ aggregates are in a global good agreement with the above men-
tioned observations, i.e., for sources presenting a high column density of sp³ hybridised carbon atoms. The bands assigned to polycyclic aromatic hydrocarbons at 3.28 and 6.28 μm (Chiar et al. 1998, 2000, 2013) are not present in the infrared spectra of both a–C:H films and ‘fluffy’ dust. The fraction of saturated aliphatic hydrocarbon groups and the hydrogen content are variable for all materials proposed as dust analogs. A suitable analog to interstellar hydrogenated carbon grains should have the hydrogen content that matches into the range arising from astronomical observations, as detailed by Dartois et al. (2007): from 19% to 42% (or hydrogen-to-carbon H / C ratio ≈ 0.23 to 0.72). Post-synthesis processing of analogs is a suitable strategy to match the above mentioned range. For example, by exposing the analogs to different external agents i.e. hydrogen bombardment (Mennella et al. 2002a,b), the hydrogen content is diminishing and might be situated in the range 20% to 42% (H / C ≈ 0.25 – 0.72).

The H / C value is highly dependent on the relative ratio of aromatic-to-aliphatic groups in the laboratory interstellar dust analogs. For an ideal aromatic network the H / C goes to zero and cannot exceed 1.6 (or hydrogen content not greater than 61.5%) (Jones 2012a) for a fully aliphatic stable network. According to Jacob & Unger (1996), for a soft polymer-like film, with a density of 1.2 g cm⁻³, the H / C ratio is around 1. The same values of density and H / C ratio were assumed by Godard et al. (2011) for a–C:H films with the refractive index of 1.4 and later on by Maté et al. (2016) for hydrogenated amorphous carbon (a–C:H) with variable mixtures of aromatic and aliphatic groups. On soot samples, polyaromatic cross-linked by aliphatic bridges, Godard et al. (2011) found a higher density (1.8 g cm⁻³), refractive index 1.7 and a much smaller hydrogen content (H / C = 0.01) than a–C:H films. The hydrogen density is higher in the aliphatic bridges that link the aromatic units and this explains this small value of H / C ratio.

Although the precise H / C ratio of the our a–C:H films and ‘fluffy’ aggregates is not experimentally known, we may use the theoretical results of Jones (2012a) to estimate the H / C ratio for high aliphatic networks. For an a–C:H film with CH₂ / CH₃ fraction approximately 1, the hydrogen content is ≈ 58% (H / C ≈ 1.4). For the ‘fluffy’ aggregate, the CH₂ / CH₃ ratio is approximately 2, that gives the hydrogen content ≈ 55% (H / C ≈ 1.2). As expected for an aliphatic sample, the ‘fluffy’ dust is highly hydrogenated. Considering also the 10% of olefinic components in the ‘fluffy’ dust, the hydrogen content will slightly decrease (Godard et al. 2011) to an estimated rough value of 50% (H / C ≈ 1).

We note now the necessity of post-synthesis processing for the ‘fluffy’ carbon aggregates, in order to reach a value of the H / C ratio in good agreement with the astronomical observations.

Along with the infrared absorption features and the specific H / C ratio of dust analogs, the mesoscale appearance should be also of interest for astronomers, to match the physical properties of dust in interplanetary space. The analysis of dust samples obtained from nearby Earth collecting flights (Messenger 2002; Mautner et al. 2006; Rietmeijer 2007), return missions carrying appropriate dust collectors (Brownlee et al. 2006; Flynn et al. 2006; Keller et al. 2006; Sandford et al. 2006; Westphal et al. 2014) or the more recent analysis of thousands of dust grains with the on-board instruments on ROSETTA orbiter (i.e. optical atomic force microscopes (Bentley et al. 2016; Langevin et al. 2016; Ellerbrock et al. 2017), showed that the interplanetary, asteroidal and cometary dust particles present some common morphological features:

- non-regular shapes and extremely diverse size distribution;
- variable degree of porosity and density, from compact particles (i.e. non-porous, smooth, crystalline structures) to highly porous structures (i.e. loosely packed, ‘fluffy’ grains);
- a hierarchical structure of clusters or aggregates, with individual sub-micron grains, of about 500 nm or less, stacked together into larger structures, with typical dimensions from 10 microns to several hundred microns;
- various types of clusters have been pointed (i.e. shattered clusters, glued clusters and rubble piles) based on the analysis of some morphological characteristics (e.g. the connecting matrix, if any, supposedly containing carbonaceous matter, the spatial relationships between components and their size distribution).

Some of the above mentioned morphological features of interplanetary, asteroidal and cometary dust particles, which already reproduced in laboratory dusty plasma experiments (Garscadden et al. 1994; Szopa et al. 2006).

Thus, an Earth based experiment aiming to synthesize dust analogs in general and more specifically an interstellar carbon dust analog, should address at least the following issues: the relationship between the spectral properties and the chemical structure (i.e. the aliphatic vs. the aromatic content), the microscopic appearance of the product and the dust analog processing due to ionizing radiation fields or highly energetic particles bombardment.

The ‘fluffy’ microscopic appearance and the hierarchical organization of the dust analog deposited onto flexible graphite substrates is consistent with the above described recent observations of interplanetary, asteroidal and cometary dust.

We conclude that the high power impulse dielectric barrier discharge in helium and hydrocarbon gas mixtures is a suitable new method for low temperature deposition of carbon dust analogs, in form of both non-aromatic thin films and ‘fluffy’ aggregates. The ‘fluffy’ carbon aggregates combine both, spectroscopic and morphological features of carbon cosmic dust, being suitable for laboratory mass production and ready for use in dust processing studies with radiations and particle beams.

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