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REVIEW ARTICLE

Interstellar Carbonaceous Dust and Its Formation Pathways: From an Experimental Astrochemistry Perspective

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Abstract | Carbon because of its electronic structure can formulate several types of bonds and allotropes. In the ranking of elements in the Universe, carbon is the fourth most abundant after H, He and O. To date, carbon signatures have been detected in different parts of the interstellar medium (ISM), circumstellar medium (CSM) and in our solar system. It is now evident that in the ISM, carbon is present in the form of gas, ice and dust phases. Almost a decade ago, astronomers were able to trace the signature of the largest carbonaceous molecule, fullerene in different parts of the ISM, including planetary nebula (PNe), reflection nebula, and in ionised hydrogen (HII) regions. This has led the growing international astrochemistry community to revisit the formation pathways of different carbon nanostructures under simulated interstellar conditions. The aim of this article is to review and summarise all the experiments relevant to the formation of interstellar carbonaceous dust performed by various groups across the globe.

1 Introduction

1.1 Carbon in the Universe

Molecules have been routinely detected at different parts of our galaxy, and to date, about 300 molecules (CDMS)[1] are known to be present. A large fraction of these molecules contain carbon (C), signifying carbon's important role in our Universe's chemical enrichment processes. Unlike H and He, C originates from stellar nucleosynthesis at the core of intermediate-mass stars. The reaction in which three ^{4}He nuclei fuse to form ^{12}C in the core of a star (AGB, red giant star) is known as the triple-alpha process[2]. Later, C is transported into the outer envelope of stars by the convection-induced degrade-up mechanism, and a tussle between the O and C is initiated. The least abundant element between them is considered locked up in the form of CO, whereas the abundant one contributes to the formation of varieties of molecules and dust. If the C/O abundance ratio is more than 1, then the observed molecules are mostly carbonaceous, whereas in the opposite case, oxides are known to dominate[3]. The abundance of C available for chemical reactions is usually measured by taking the difference between the cosmic abundance of C to H $[C/H]^{c}$ and the gas-phase abundance of C to H $[C/H]^{g}$[4]. To date, the known cosmic C abundance is around 85-C atoms per 10^{6} H atoms, whereas, in the Sun's photosphere, it is about 250 C atoms per 10^{6} H atoms[4].

Due to its ability to make different kinds of bonds, C has contributed to the ISM's molecular enrichment, especially by synthesising organic molecules. Targeted multi-wavelength astronomical observations towards different astrophysical sites reveal the presence of various organic and inorganic carbonaceous molecules and radicals. These range from the simplest diatomic molecule, CO, to polyatomic aliphatic sp^{3}-bonded alkanes such as CH_4, sp^{2}-bonded alkenes such as C_2H_4, the sp-bonded linear C_2H_2, and long-chain

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hydrocarbons such as polyenes and cyano-polyenes. The presence of large aromatic molecules in different parts of the ISM was proposed in the mid-80s, and their signatures have been found in various astrophysical objects[5]. Signatures of benzene in stellar envelopes were detected almost two decades ago[6]. Large molecules made of multiple benzene rings are called polycyclic aromatic hydrocarbons (PAHs), with almost 20% of the cosmic carbon being thought to be locked up in such molecules[5]. However, detecting specific PAHs in the ISM has been difficult, at least until recently, when benzonitrile was discovered in the dark molecular cloud TMC-1[7]. Since then, many other smaller PAH molecules have also been reported to be present in TMC-1; these include 1-cyanonapthlane, 2-cyanonapthlane[8], and indene[9,10]. A detailed survey of different molecules and radicals which are reported to be present in the ISM, CSM and extragalactic environment can be found in the recent census carried out by McGurie and co-workers[11]. Many carbon-bearing molecules (gas phase) are thought to be potential carriers of different unknown spectroscopic features detected in other parts of the ISM. The well-known Unidentified Infrared Emission features (UIE) have the most robust IR features around 3.3, 6.2, 7.7–7.9, 8.6, 11.3, and 12.7 μm. These bands are called aromatic infrared bands (AIB) and are attributed to PAHs[5,12,13]. Finding a suitable carrier for the Diffuse Interstellar Band (DIB), a weak absorption feature spanning 400–1200 nm, has been an unsolved problem for the Astronomy/Astrochemistry community. However, the ionic fullerene ($C_{60}{}^{+}$) molecule may solve this interstellar puzzle. The experiment conducted by Campbell et al. (2015) and Linnartz et al. (2020) showed that two of the DIB's bands, around 9632.7 Å and 9577 Å are due to $C_{60}{}^{+}$. Formation pathways of carbonaceous molecules are still an evolving topic and beyond the scope of this paper and further discussions can be found elsewhere in the literature by Henning and Salama[4] and the references therein.

Dust accounts for only 1% of the interstellar mass budget, despite that its importance in interstellar chemistry cannot be ignored. Submicron to nanometer size dust grains are ubiquitously detected in various parts of interstellar space and in our solar system. The chemical composition of dust in different parts of the ISM as well as in our solar system has been probed using space-borne infrared (IR) telescopes such as the Infrared Space Observatory (ISO), followed by Spitzer, and airborne observatories like the Stratospheric Observatory for Infrared Astronomy (SOFIA)[14]. On the other hand laboratory experiments suggest that geometrically shaped dust particles may be a key component of interstellar dust[75], and analysis of meteorites have revealed morphological information and isotopic composition of the dust[14]. Solid matter in interstellar space can be divided into three broad categories: first, refractory mineral dust such as olivine, pyroxene, and other metal oxides. Second, solid carbonaceous dust, such as SiC, and other carbon allotropes, such as diamond, graphite, amorphous carbon, and fullerenes, a more recent addition to the inventory. The third and final member of this classification is molecular ice, which is composed of volatile abundant molecules such as CO, H_2O, CH_4, and some PAHs[15]. Interstellar carbonaceous dust manifests its presence through various spectroscopic features in different wavelengths, and their morphology, internal structure, and the nature of chemical bonds influence their spectral properties. In the UV region , the presence of carbon-containing dust can be traced by studying the interstellar extinction feature around 217.5 nm[16,17]. The transition between π and π* of the hydrogenated carbonaceous dust has been proposed to be the carrier of such a feature. The UV absorption feature around 240–250 nm observed in different H-poor objects has also been attributed to the π to π* electronic transition of hydrogen-poor carbonaceous dust[18,19]. Signatures of H-poor amorphous carbon dust are also found around many carbon stars by studying the featureless continuum infrared emission[20]. The Extended Red Emission feature (ERE) peaking at 650 and 700 nm, has been detected around different interstellar objects[21,22]. The UV-induced luminescence of hydrogenated amorphous carbon (HAC) has also been suggested as an explanation of this emission feature. A recent experimental result by Sarre[23] has shown that graphene oxide nanoparticles could also contribute to the ERE features. Although graphene has not been detected in interstellar space, the presence of C_{24} planer sheets is claimed in the planetary nebula[24]. In addition a recent experiment that irradiated a benzonitrile ice film at 4K using 9eV photons, followed by gradual warming to room temperature demonstrated the formation of nitrogen doped graphene sheets, suggesting a possible pathway for the formation of graphene in the ISM[76]. The well-known 6–9 μm plateau emission features and 3.4 μm absorption features are also assigned to hydrocarbon dust particles. Although UV pumping of PAH, followed by IR fluorescence, is a well-accepted mechanism to explain the UIE features in IR, an alternative explanation exists. Mixed aliphatic aromatic organic nanoparticles

(MAONs), which contain different mixtures of sp^2- and sp^3-bonded hydrocarbon networks, can also explain the UIE features[25]. Fullerene is the most recently detected component of cosmic carbon dust. Its infrared active features around 7.0, 8.5, 17.4, and 18.5 μm have been detected around planetary nebula[26], reflection nebula[27,28], diffuse ISM[29], and around young stellar objects like Herbig Ae/Be stars[30]. The other spectroscopic feature in IR, which shows the presence of carbonaceous dust around C-rich stars, is the 11.3 μm feature, which has been attributed to the SiC[31]. A detailed description of the known carbonaceous dust detected in space can be found in the review article by Dartois[15]. The James Webb Space Telescope (JWST) is now fully operational and its capability both in the near IR (NIR) and the mid-IR (MIR)[32] is expected to add greatly to our present knowledge of interstellar carbon dust.

Signatures of interstellar carbon dust have also been detected in primitive meteorites as presolar grains. Presolar grains are known to have originated well before our solar system's formation and contain valuable information about their respective birth site in the proto solar system. The most abundant carbonaceous presolar dust is nanodiamond the second most abundant is SiC, followed by graphite[33]. The isotopic anomalies present in the presolar grains make it unique from other solar system grains. By studying the isotopic anomalies of Xe and Kr present in the Allende meteorite C3V chondrites, cosmochemists were able to detect presolar nanodiamonds [34]. Later, Chang et al.[35] and Guillois et al.[36] reported the presence of nanodiamonds around intermediate-mass stars. They attributed the 3.43 and 3.53 μm IR features to the C–H stretching motion of the hydrogenated nanodiamonds. The signature of presolar SiC was first detected in the Murray carbonaceous chondrite[37].

2 Dust Formation in the Astrophysical Environment

Dust is known to be produced in the extended envelope of stars. These include low to intermediate-mass (0.8–10 solar mass) stars such as asymptotic giant branch (AGB) stars, red giants and supergiant stars. At the end phase of stellar evolution, these stars make extended cool envelopes where the dust-forming elements (C, O, Mg, Si, Fe, etc.) are mixed according to their abundance[38,39]. The condensation of dust in the stellar envelope is a very complex process, which starts from molecular mixtures in the gas phase, and molecular clusters are made after a series of chemical reactions. The subsequent growth of molecular clusters makes a solid dusty seed, which provides a finite surface for further dust growth[39]. The thermodynamic conditions, elemental mixing, metallicity and stellar radiation field influence the sequence of dust condensations, which in turn affect the structure, morphology and spectral properties of dust grains. A combined effort of theoretical and experimental studies is required to understand the entire formation pathway of dust, including information about the molecular precursors, intermediate products, and various possible end products.

To date, there exist two different formation pathways of interstellar carbonaceous nanodust. These are 'bottom-up' formation routes that mimic dust formation from the atomic and small molecular precursors and 'top–down' routes—where dust formation happens because of the destruction of larger molecular clusters. Each of these processes has advantages and limitations. This review mainly focuses on laboratory experiments on the formation of carbon nanodust carried out by different laboratory Astrochemistry/Astrophysics groups across the globe.

2.1 *Laboratory Formation of Carbonaceous Dust via Bottom–Up Route*

Experiments dealing with the bottom–up formation process of carbonaceous dust grains in interstellar space mostly mimic gas-phase condensation events in a simulated circumstellar environment. Principally these kinds of experiments are done in two steps. The first step is the production of vapour of any atomic or molecular precursor material through pyrolysis or sublimation. This can be carried out using various energetic sources such as a laser, arc discharges, and shock tubes. In the second step, the produced vapour can settle on a substrate or can be directly quenched in a cool inert gas environment[40]. A pictorial representation of the possible pathways of carbonaceous dust formation can be seen in Fig. 1. A detailed discussion of different laboratory techniques used to produce cosmic carbon nanodust grain analogues follows.

2.1.1 Laser-Induced and Graphite Reactor-Based Pyrolysis

Laser-induced pyrolysis of the gaseous precursor is a promising technique to produce a cosmic carbon nanodust analogue. In this method,

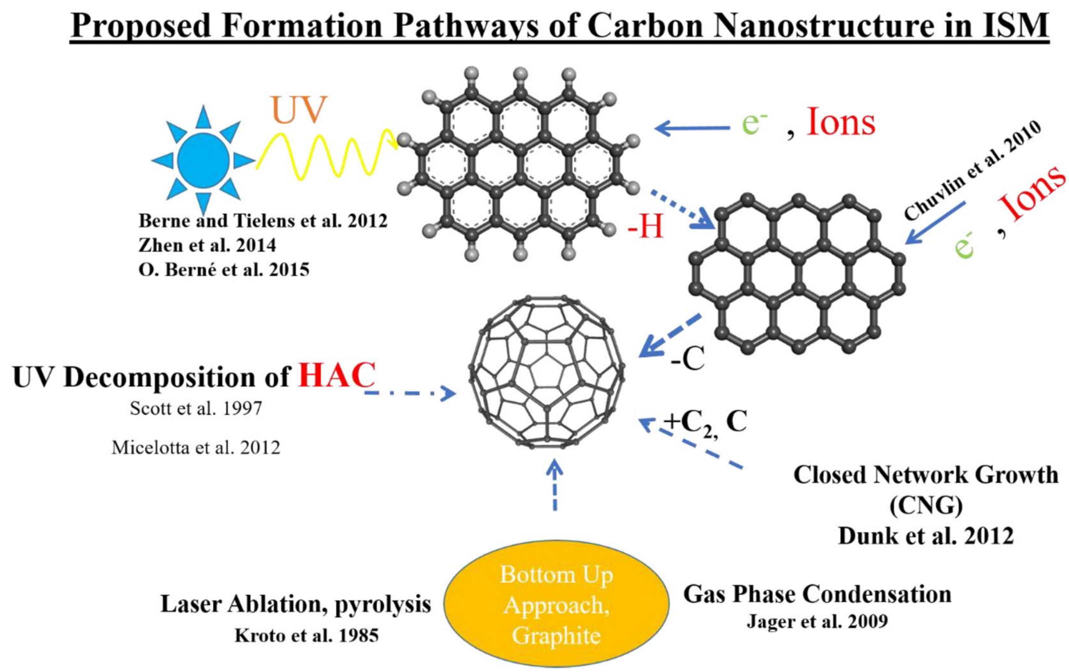

Figure 1: Proposed formation pathways of carbon nanodust in the ISM.

the gas-phase precursors molecules are rapidly heated and dissociated using either continuous wave or pulsed laser. To do so, the precursor molecule or molecular mixtures should absorb the laser radiation; else, a sensitizer like sulphur hexafluoride SF_6 (for CO_2 laser) is usually used. The soot particles produced from the pyrolysis of the precursor can be collected using particle filters or allowed to nucleate on any substrate far from the reaction zone. A flow of inert gas such as Ar and N_2 has been used to move the produced dust particles. The presence of a well-defined and relatively small reaction zone and sharp thermal gradient helps to control the nucleation rate and laser interaction time. This provides an advantage over conventional techniques such as the plasma-heated gas-phase process or furnace-based techniques[41,42]. The factors which influenced the nature of the carbon dust produced in this method are the nature of the precursor, the pressure of the reaction chamber, laser intensity and the residence time of the gas-phase molecules in the laser beam, which depends on the mass flow rate of the gas mixture.

Using this technique, the condensation of diamond nanoparticles at low pressure (1000 mbar) and temperature (500–550 °C) has been investigated by Buerki et al.[43]. They used two sets of gas mixtures, pure C_2H_4 and mixtures of C_2H_4, H_2, and SiH_4 and decomposed these mixtures using a CO_2 laser (10.6 µm, 6000–8000 W cm^{-2}). Diamond's cubic and hexagonal phases and polymeric hydrocarbon species, amorphous carbon and graphite were observed. Nucleation of nanodiamonds in the low-pressure condition can complement the diamond formation theory in the ISM suggested by authors such as Lewis et al.[34], Anders[44], and Jørgensen[45].

The formation of carbon nano-grains mimicking the thermal decomposition of C_2H_2 in evolved carbon star atmospheres has been experimentally investigated by Herlin et al.[42]. A continuous wave CO_2 laser operating at a wavelength of 10.6 µm and with powers ranging from 200 to 1000 W was focussed perpendicularly on two different molecular beams of C_2H_4 and C_4H_6. The range of the parameters used in this experiment are the gas flow rate ~ 30 to 540 cc min^{-1}, pressure ~ 700 to 900 torr, laser power 280–450 W, and the estimated temperature range was around 1200–1500 K. TEM analysis of the high-temperature condensate (~ 1500 K) revealed the presence of spherical particles (20–40 nm) with organised internal structure and their IR spectra showed the presence of a strong continuum. This suggests that these high-temperature condensate dust grains have poor hydrogen content. The low-temperature condensate is mainly dominated by amorphous carbon, and its IR spectra have features of aromatic –CH and –C–C vibrational motions [42].

Unlike Herlin et al.[42], who used a continuous wave CO_2 laser, Schnaiter et al.[46] used a pulsed CO_2 laser to study the formation of interstellar carbon dust analogues from C_2H_2. As C_2H_2 does not absorb 10.6 µm radiation, they mixed the gas with sulphur hexafluoride (SF_6) as a sensitizer with different concentrations, which plays a key role in determining reaction temperature up to as high as 2000 K. The produced soot particles were extracted using a mass filter attached to the pumping line. The produced materials were analysed using techniques such as IR spectroscopy, TEM imaging electron energy loss spectroscopy (EELS), and time of flight (TOF) mass spectrometry. One of the major findings from this experiment was the growth of PAH during the nucleation of amorphous soot particles.

Biennier and co-workers[47] produced carbonaceous dust by pyrolysis of the gaseous precursor acetylene in a chamber with reduced dimensions known as circumstellar carbon analogue source. It is a high-temperature reactor, and its dimension reduction was achieved using a heated porous graphitic rod. This rod can be heated electrically to a temperature of the order of 2000 K. Because of its porosity the rod has a large exchange area, allowing for efficient heat transfer from the rod to the gas flowing through it. The thermodynamic conditions under which acetylene pyrolysis occurred were comparable to those in circumstellar shells. The condensed particles were analysed using nuclear magnetic resonance (NMR) spectroscopy, XRD, and IR spectroscopy. The NMR result showed the presence of smaller aromatics in the soluble components of the pyrolysis product. XRD analysis of the bulk samples showed the presence of amorphous chemical networks, which contain small organised aromatic islands composed of two graphene layers connected by aliphatic groups. The IR spectra of the condensate showed aromatic features around 3.29, 6.30, 11.36, 11.98, and 13.31 µm. The broad 7.7–10 feature has also been assigned to the aromatic CC and CH plane deformation motions. Signatures of aliphatic groups were also observed at 3.42 and 3.50 µm. The aromatic-to-aliphatic ratio almost remained at 3.2 for the entire sample. The IR spectra of the condensate showed a strong resemblance to some IR emission spectra of the post-AGB stars observed by Dartois et al.[48].

2.1.2 Laser Ablation of Graphite

Laser ablation of solids is another technique routinely used to produce cosmic dust analogues under laboratory conditions. The vapour produced in this method can be rapidly quenched in a low-pressure (1–25 mbar) inert gas atmosphere (He/Ar) with a rate as high as 10^4 K s^{-1}. This leads to the formation of soot particles, which can be extracted from the laser ablation chamber by injecting them into a molecular beam using a nozzle and skimmer. The condensate's physicochemical nature depends on the laser pulse energy and quenching gas's thermodynamic properties. Different experiments have been carried out using various precursors and the parameters such as chamber pressure, laser intensity and wavelength.

One path-breaking experiment using the laser ablation technique was carried out by Kroto et al.[49] and led to the discovery of a new carbon allotrope fullerene (C_{60}). This experiment aimed to understand the formation mechanism of long carbonaceous chains in the envelope of the evolved AGB stars. Graphite was vaporised using a Nd: YAG laser with pulse energy ~ 30 mJ. While expanding with supersonic speed, the vapour was photo-ionised utilising an excimer laser and analysed using TOF mass spectrometry. Pressure played a key role in this experiment. When the quenching gas pressure was low (less than 1300 Pa (10 torr)), wide ranges of carbon clusters were detected, starting from C_{30} to C_{120}. At a pressure of ~ 101325 Pa (760 torr), both C_{60} and C_{70} peaks were visible and distinguishable. Under the same experimental conditions, passing the carbon vapour through an integration cup caused He-cluster, cluster- cluster collision and only the stable clusters survived. The mass distribution under this condition was dominated by C_{60} (50%) and C_{70} (5%) as the surviving clusters. The structure of C_{60} was predicted to be like a football, and later it was spectroscopically confirmed by Krätschmer et al.[50] and Dennis et al.[51].

Laser-induced ablation of graphite in He, He + H_2 environments was experimentally studied by Jäger et al.[40]. The pressure of the quenching gas varied between 3.3 and 26.7 mbar, and the laser-produced plasma with a temperature range between 4000 and 6000 K was produced. Fullerene and fullerene-like soot were observed in the high-temperature condensates.

Fulvio and co-workers[52] have studied the low-temperature formation of carbonaceous grains from graphite. With the help of a Nd:YAG laser (wavelength 532 nm, 10 pulses per second, 10 mJ of energy), graphite pellets were ablated. Vapours created because of laser ablation were allowed to settle on a cold (~ 10 K) KBr substrate directly or in an Ar ice matrix. The chemical composition of the condensate grown on top of the KBr substrate or isolated within the Ar ice matrix was probed using UV and mid-IR (MIR) spectroscopy, and the morphology of the condensate was studied using field emission scanning electron microscope (FE-SEM) and high-resolution transmission electron microscope (HR-TEM). This confirmed the presence of carbon clusters of different sizes starting from C_2 to C_{13}, although a few oxidised species such as CO and C_3O, and possible contaminations from H_2O and CO_2 have also been noticed[52]. The FE-SEM images of the condensate showed the presence of meshed structure with a dimension of the order of a few µm. The HR-TEM images demonstrated a fullerene-like structure with different sizes and shapes. In the second part of this work, they carried out successive vacuum ultra violet (VUV) irradiation on the condensate to understand the effect of energetic processing on the dust grains during their growth in interstellar conditions. As a VUV source, they employ a microwave powder hydrogen discharge lamp with two prominent spectral features at 122 and 160 nm. The effect of VUV irradiation on the physicochemical properties of the condensates was probed using MIR spectroscopy, FE-SEM, and HR-TEM imaging techniques. A drop in the intensity of MIR bands corresponding to different carbon chains and clusters has been observed. This showed that under VUV irradiation, these carbon chains and clusters were fragmented. These fragmented products reacted with themselves and made fullerene-like structures, observed in HR-TEM images. These fullerenes-like structures were much more ordered than those observed in the non-irradiated condensate[52]. The presence of a chain-like structure in the low-temperature condensate was previously in the reported high-temperature condensate by Jäger et al.[43]. These chain-like structures were also proposed to serve as an intermediate product for the fullerene and fullerene-like particle growth in the atmosphere of Wolf Rayet stars[53].

2.1.3 Dust Production Using Combustion in Flames

Combustion of gas-phase hydrocarbons mixed with oxygen is another method to produce cosmic carbon dust analogues. The nature of the soot particle produced in this technique depends on various factors such as chamber pressure, the flame's temperature, the precursor molecules used, the C/O ratio and the construction of the burner[54]. In this technique, soot particles can nucleate at low pressure and can be extracted using a quartz cone or nozzle [55]. This technique uses different types of hydrocarbons to produce carbon dust, e.g. CH_4, C_2H_2, C_2H_4, C_3H_6, and C_6H_6. These hydrocarbons were decomposed in different C/O ratio environments (0.5–2), and the flame temperature was as high as 2500 K[56]. A range of end products has been reported to form, including long carbon chains, PAHs, and fullerene-like particles[56].

Carpentier et al.[57] have also investigated the structural and spectroscopic properties of cosmic carbonaceous dust analogues produced from precursors such as ethylene and propylene using the same setup used by Pino et al.[53]. Here, both the precursors were burned using a flat flame in a fuel-rich environment, where the C/O ratio was in the range of 1.1, 1.4, and 1.6 for all three sets of experiments. Soot particles were allowed to deposit on a stainless steel substrate and analysed using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and HR-TEM imaging techniques. Variations observed in the IR absorption feature, especially in the 6.2 µm and 7.7 µm region of the soot particles, have also been reported to be present in the IR spectra of the interstellar carbon dust. This could be due to defects and polyaromatic structures in the soot particles, verified using techniques such as HR-TEM imaging and Raman spectroscopy. Based on these results, plausible scenarios for carbonaceous dust growth in the ISM have been proposed, which are discussed in detail in Carpentier et al.[57].

2.1.4 Microwave, Radio and Arc Discharge Technique

Condensation of carbonaceous dust can also be studied using the microwave discharge plasma technique. In this technique, gas-phase molecular precursors such as CH_4 fill a quartz tube exposed to a magnetron's microwave field. This causes methane dissociation, and the ionised gas is passed into a vacuum chamber, where it condenses into black soot particles. X-ray (XRD) diffraction and UV spectroscopic analysis of the condensate reveal the presence of quenched carbonaceous composites (QCC). UV spectra correlate well with the interstellar extinction curve, peaking around 2200 Å[58]. Using the radio frequency plasma technique, spherical carbonaceous grains have also been produced from C_2H_2[59]. The arc discharge technique has also been utilised to produce carbon nanoparticles. One of the important results of this kind of experiment was the discovery of carbon nanotubes by Iijima[60]. Mass production of fullerene has been developed using this technique[50]. In such experiments, closed network growth (CNG) leads to the bottom–up formation of fullerenes by inserting C and C2 in smaller cages[61]. Similar bottom–up routes lead to the formation of CNTs also[62].

2.1.5 Production of Cosmic Grain Analogue from Gas-Phase Molecular Precursors Using Plasma Chemistry

Cosmic carbonaceous dust analogues, their formation and evolution can also be studied experimentally under simulated interstellar and circumstellar conditions using NASA's COsmic SImulation Chamber (COSmIC)[63]. COSmIC has three major components: a pulsed discharge nozzle (PDN) capable of producing microscopic particulates by exposing a supersonically fast Ar jet seeded with precursor molecules like PAHs and other hydrocarbons to a plasma discharge. The products generated in this hot plasma experience rapid cooling over a very short distance as the plasma expands. Second, a cavity ring breakdown spectrometer is attached to the system to probe the spectroscopic information of the products. Third is the orthogonal reflection time of flight mass spectrometer (TOFMS) for studying particulates' mass and structural information[63].

Using COSmIC, Contreras and Salama investigated the formation of circumstellar carbonaceous dust analogues from different aliphatic and aromatic molecular precursors. These include methane, ethane, ethylene, and acetylene representing aliphatic precursors. For the aromatics, the precursors were benzene, toluene, pyridine, and different PAHs. Results from these experiments showed that the nature of the end product has a high dependency on the molecular nature of the precursors. This fact has to be considered in the theoretical models dealing with dust formation in circumstellar conditions. The fragments generated from aliphatic precursors and small-ring molecules such as benzene, toluene and pyridine have shown a tendency to recombine and enhance molecular complexity via ion-molecular reactions. Such molecular growth can lead to grains forming in the circumstellar environment via chain growth and ring formation[63]. Homogeneous (naphthalene, 1-methylnaphthalene, and acenaphthene) and heterogeneous (quinoline, benzofuran, and thianaphthene) PAHs used in this experiment showed better stability and did not contribute to any chemical reaction which led to the formation of dust grains[63]. Results from this experiment were found to support the assumptions considered in the models [64] made to describe PAH formation in the circumstellar environment, where the interaction among the propargyl (C_3H_3) radicals led to the formation of benzene and then the growth of larger aromatic molecules started via the so-called hydrogen abstraction and acetylene addition (HACA) mechanism[65].

Using the COSmIC facility, Gavilan and Salama [66] explored the low-temperature (<200 K) formation pathway of carbonaceous dust from PAH, starting from benzene, naphthalene, anthracene, phenanthrene, and pyrene. Condensates generated separately from these PAHs were collected on a substrate (graphite bar) and analysed using laser desorption mass spectrometry. Mass spectra obtained from these condensates showed the fragmented part of the precursor molecule and the signature of the larger complex organic molecules. Pyrene, its isomers, and its methylated series were the most abundant product in all condensates originating from the above mentioned PAHs. This indicated a favourable pathway for the formation of larger PAHs and solid grains via the formation of stable PAHs such as pyrene and its isomers. The dust formation yield was maximum when using anthracene, whereas for the benzene, it was a minimum. The absence of heavy masses (>400 m/z) showed that the solids grains were not refractory; instead, they were mostly made of organic molecules, mainly medium size aromatics, connected via aliphatic bonds. As the residence time of the precursor molecule in the plasma was limited by a few microseconds, the growth and the formation of molecules within these solid grains could be a good representative of the early PAH growth mechanism. This work has also studied the effect of the precursor's structure on PAH growth. This was explored using anthracene and phenanthrene, where anthracene dissociated more effectively in the plasma and phenanthrene demonstrated greater thermal stability. The dust production yield in the case of anthracene was almost six times that compared to phenanthrene. However, the mass spectra of the condensate from these two isomers were similar, indicating that dust generated from these two isomers followed the same kinds of growth mechanism and was independent of the precursor's dissociation cross-section. A comparison of the mass spectra between the condensate from anthracene and the Murchison meteorite showed a preponderance of pyrene, its isomers and methylated products in both instances. This suggests a possible low-temperature formation of PAHs in the parent body of the Murchison meteorite [66]. Also, it is important to note the growth of small and medium size PAHs within the solid grains, which could save them from destruction by extreme interstellar energetics; these PAHs can be released in the gas phase by various dust destruction processes like stuttering.

Sciamma-O'Brien and Salama[67] studied the morphology of the dust grains produced in the COSmIC facility using the precursors such as methane and acetylene. The grown carbonaceous grains were collected on a Quantefoil grid and analysed using a FE-SEM. The size and shape of the carbonaceous grains were found to be different for different precursors. For the methane, the grains were in the diameter range from 15 to 385 nm, with an average density of ~ 2.1 grains μm^{-2}. In contrast for the acetylene, the grains showed much spherical structure compared to grains formed from methane, and these grains had a diameter in the range of 40 to 650 nm with an average density of ~ 3.5 grains μm^{-2}. This morphological change of the carbonaceous grains can be linked with the different stages of dust growth at low temperatures. The planer structure grows first and then coagulates into a spherical form[67].

Raman spectroscopy is now part of many ongoing and future planetary exploration missions. PAHs have delocalized pi-electrons, which enhances their polarizability and makes it an excellent target to probe using Raman spectroscopy. Gavilan and co-workers carried out a Raman spectroscopic study of microcrystalline pyrene and the dust particles derived from pyrene[68]. These dust particles were synthesised by exposing gaseous pyrene seeded in a carrier gas Ar to a pulsed (300 µs) plasma discharge (~ 1000 V) in the COSmIC facility. Raman spectra of the microcrystalline pyrene consist of many narrow bands and showed a good match with the previous studies on the single crystal and powder form of pyrene. Raman spectra of the dust particles contain a broad G band around 1580 cm^{-1}, indicating the presence of graphitic structures. Its D band has multiple components assigned to the defects present in the disordered carbonaceous dust. Gavilan and co-workers compared several Raman parameters, such as peak position, full width half maxima (FWHM), and peak intensity ratio of D to G band (I_D/I_G), between the produced carbonaceous grains and various cosmically important carbonaceous dust, such as insoluble organic molecule (IOM) from meteorites, soot, and hydrogenated amorphous carbon. (HAC). This comparison revealed that the produced carbonaceous dust grains were more crystalline than HAC, and their crystallite size was smaller than soot particles. However, a good match was observed in the crystallite size of IOM from the Allende meteorite and generated carbonaceous grains, indicating a probable low-temperature pathway of IOM in the Allende meteorite[68].

2.1.6 Low-Pressure Gas-Phase Condensation Technique

Martinez and co-workers[69] have studied the formation of cosmic carbonaceous dust analogues from gas-phase carbon atoms and molecular hydrogen with different ratios similar to the atmosphere of AGB stars. The experiment was carried out in a setup known as Stardust[70], which is an UHV system capable of mimicking thermodynamic conditions observed in the dust formation zone of many evolved stars like AGB and allows studies of the formation, evolution of dust in those conditions. Here atomic carbon was produced by means of sputtering of graphite target using Ar ion, and this atomic carbon was reacted with molecular hydrogen in a gas aggregation zone, where the gas temperature was around < 1000 K. Two different molecular hydrogen concentrations 1.5×10^{10} molecules cm^{-3}, referred as low density and 1.5×10^{10} molecules cm^{-3}, referred as high density were used in this experiment and the reactions were monitored with the help of optical emission spectroscopy (OES) technique. The gaseous reactant and products were immediately extracted into another chamber with a differential pressure using a nozzle. Here the solids present in the extracted gas were collected on a substrate, and the product remains in the gas phase analysed using quadrupole mass spectrometry (QMS) technique. The morphology of solid aggregates was analysed using a atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), whereas the chemical composition of these solid grains was studied using laser desorption ionisation mass spectrometry (LDIMS). The OES results for the low hydrogen density case showed the formation of C_2, whereas its signature was missing in the case of the high hydrogen density case. The absence of C_2 in the high hydrogen concentration case suggested that most of the C_2 was consumed in a chemical reaction $C_2 + H_2 \rightarrow CCH + H$. For the low hydrogen density QMS, the result showed the signatures of aliphatic hydrocarbons such as C_2H_2 and fragments of C_2H_4, C_2H_6, and other larger molecules. An increment in the abundance of these above mention molecules was observed with the increase in the hydrogen density. Notably, no signatures of fullerene and PAHs were noticed. AFM images of the solid particles showed a spherical shape with an average height of ~ 9 nm. STM images of the condensates showed various amorphous carbon nanostructures with heights ranging from 1 to 5 Å. Signatures of individual molecules with five carbon atoms were also predicted. The LDIMS analysis showed a larger abundance of CH clusters for low hydrogen density. The largest aromatic molecule detected in a trace amount was $C_{16}H_{10}$, suggesting that the condition in which these grains formed was unsuitable for PAH or larger carbonaceous molecules to grow. Although signatures of benzene and naphthalene were detected after the annealing of the carbonaceous grains at a temperature of more than 355 K, suggesting a possible surface catalytic reaction between smaller hydrocarbons. Such annealing of nano-grains can occur in ISM upon UV photon absorption and can lead to PAH formation through grain surface reactions[69].

2.1.7 Formation of Carbon Clusters in the Ice Phase

Molecular ices play a key role in the chemical enrichment processes of the interstellar medium. These ices are made of volatile molecules such as H_2O, CH_3OH, CH_3CH_2OH, CH_4, NH_3, C_2H_2, and PAHs[71]. In the cold, dense interstellar clouds (~ 10 K), these molecules are accreted on top of a refractory core made of silicates/carbonaceous materials. These molecular ices have gone through various non-energetic (thermal chemistry and atom addition chemistry) and energetic processing (shock chemistry, photochemistry, radiation chemistry)[72] in interstellar space. Irradiation of UV photons on the top of the ice surface can initiate photochemistry, forming new molecules and refractory organic residues[71]. Thermal processing of dust grains can sublime these ices and enrich interstellar space by releasing molecules into the gaseous phase. In contrast, the refectory organic residue can stay on the dust surface until a much higher temperature and contribute to the growth of dust grains. To understand the extent of molecular complexity forming on the top of the dust surface in the ice phase, different groups across the globe have conducted extensive lab-based work on the energetic processing of ice. A detailed review of these works can be found elsewhere in the literature by Bernstein[71] and Sanford et al.[73].

Lin et al.[74] have experimentally studied the formation of hydrocarbon and carbon clusters of different sizes from methane ice. Using a synchrotron, pure CH_4 ice and CH_4 in Ne ice matrices at ratios (CH_4:Ne) 1:100 to 1:10,000 at 3 K were irradiated using photons with wavelengthes less than 165 nm. The IR spectra of the irradiated ice showed the presence of multiple hydrocarbon species, such as CH_3, C_2H_2, C_2H_4, C_2H_6, C_4H_2, C_4H_4, C_5H_2, C_8H_2, and C_nH ($n = 1$–5), and bare carbon clusters C_n ($n = 1$–20). The yield of the hydrocarbon chain growth is found to be dependent on the energy of the irradiating VUV photon, especially when it is more than the dissociation energy of CH_4. The efficiency of the agglomeration of the carbon clusters has also been reported to be influenced by the concentration of CH_4 and the mixing of H_2 in small proportions.

Knowledge of the physical structure of the organic refractory residue made on the surface of dust grains due to the energetic processing of ice has been limited. However, Rahul et al.[75] have shown that the physical structure of the residue made on the dust surface can have a wide range of structures and shapes, from flakes to cubes to the elongated triangular prism. For example, benzene deposited on a cold (~ 4 K) LiF substrate was irradiated using 9 eV VUV photons for 9 and 25 h. After irradiation, the ice was heated with a ramp rate of 5 K min^{-1} up to 300 K. At 300 K temperature, most volatile organics are expected to be sublimated, and only a residue will remain on the substrate. VUV spectroscopy of the residue showed the presence of benzene derivatives such as aromatics and side carbon chains. FE-SEM images of the residue showed flakes, cubes, and spherical particles. After 25 h of irradiation, the observed structures are cubes, T-shaped rods and many elongated prisms-like structures. These results can help our understanding of the physical shapes and bottom–up growth of the mixed aliphatic–aromatic dust produced on top of the pre-existing dust grains in ISM.

Recently, benzonitrile has been discovered in the molecular cloud TMC-1 (McGuire et al. 2018). This small molecule and similar benzene derivatives are believed to play a vital role in forming larger PAHs in the interstellar medium.

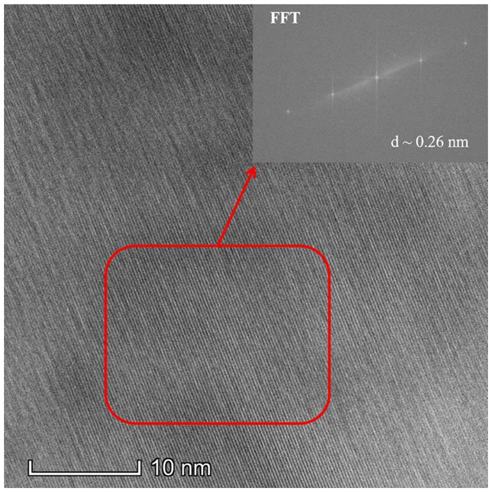

Figure 2: HR-TEM image of the VUV-irradiated benzonitrile residue. Inset is the FFT of the area marked by red rectangle. d spacing is around 0.26 nm, which is indicating the presence of graphene in the irradiated residue.

The fate of benzonitrile in the cold interstellar icy conditions (4 K) exposed to the VUV photons has been experimentally investigated by Sivaraman et al.[76]. Irradiation of benzonitrile ice at 4 K using 9 eV photons produced refectory organic residues, which remain on the substrate even after heating up to 300 K. HR-TEM, electron-dispersive X-ray (EDX) analysis of the residue has shown the presence of N-doped graphene and graphene quantum dots. The fact which makes this experiment unique is that it showed carbon nanodust graphene (Fig. 2) and quantum dots (Fig. 3) could be made in cold icy conditions. These results can also be relevant for the atmospheric chemistry of Titan, where nitrogen and PAHs are known to be present.

The simultaneous formation of carbonaceous and silicate grains in cryogenic conditions on a pre-existing dust surface was experimentally studied by Rouillé et al.[77]. In neon ice matrices, atomic (Mg, Fe) and molecular precursors (SiO, SiO_2) of silicates and carbonaceous dust (C_n, $n = 1$–20) were initially doped. By annealing these doped atomic and molecular precursors interact with each other and showed the evolution of a Si–O stretching feature around 10 μm, below 13 K. A broad 10 μm feature showed the presence of amorphous silicates. TEM and EDX analysis of the solid refractory residue showed that amorphous carbon and silicate are condensed together, although they are chemically different. These experimental results validate that silicates and carbonaceous materials can be reformed in cold interstellar conditions.

3 Top–Down Formation Pathways

While bottom–up formation routes can produce large quantities of fullerenes and other carbon nanodust, they require high temperatures and densities. Therefore, it is questionable that such processes are efficient in the tenuous diffuse ISM, which is why top–down formation pathways should also be considered. As the name suggests, this formation pathway can be started with the larger PAH molecules (>50 C atoms)[78,79] or graphene[80] or HAC[81,82], SiC[83,84]. A pictorial

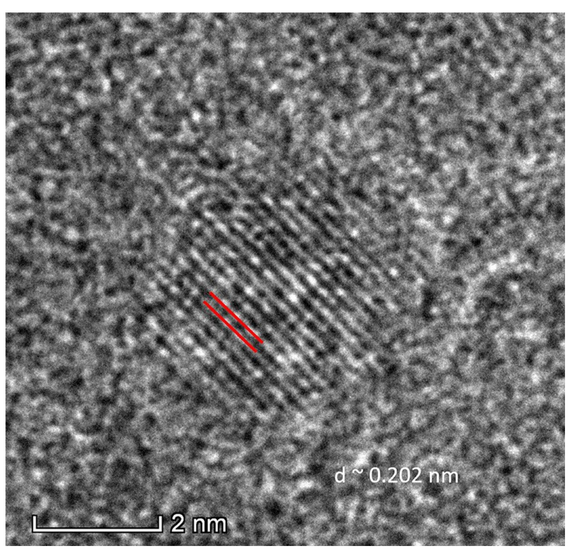

Figure 3: HR-TEM image of the graphene quantum dot with d spacing ~ 0.202 nm in the VUV-irradiated benzonitrile residue.

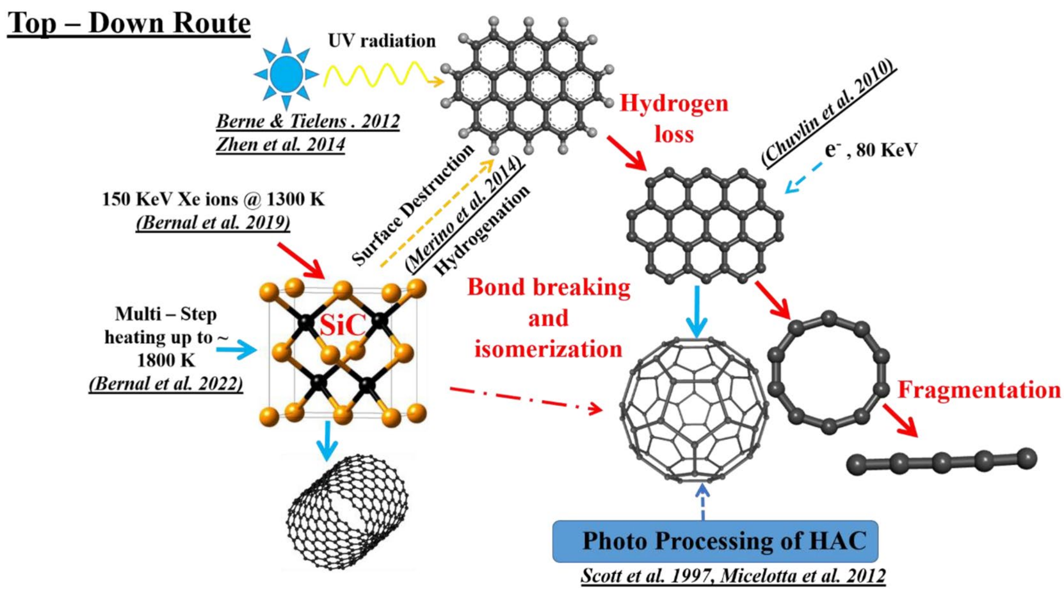

Figure 4: Schematic representation of carbonaceous dust's top–down formation route in the ISM through the destruction and fragmentation of larger carbon-rich molecules and grains.

representation of the various known/proposed top–down formation route of carbon dust in the ISM can be found in Fig. 4.

Direct formation of fullerene from graphene was first experimentally demonstrated by Chuvilin and co-workers[80]. In this experiment, graphene was placed in an aberration-corrected TEM and irradiated using an 80 keV electron beam. Exposure of the graphene to the energetic electron beam led to the removal of C atoms from its edge. At the same time, these high-energy electrons also destroy the graphene sheets producing many small graphene flakes by means of energy transfer to the carbon atoms. As time progressed, more energy was deposited on these small flakes, and their shapes started changing to round shapes. The end product is often observed to be perfect fullerene. The sequence of the transformation of graphene to fullerene can be understood in 4 steps. In the first step, the carbon atoms at the edges of the graphene sheet were removed. In the second step, the formation of the pentagon started to form to minimise the energy of the dangling bonds. In the third step, several pentagons come together and form bowl-like structures, and in the final stage, these bowl-shaped structures combine to form fullerene.

Berné and Tielens[78] proposed the top–down formation of cosmic carbon dust, especially fullerenes, by photochemical processing of larger PAHs. Spritzer observations of the PNe NGC 7023 showed the co-existence of PAHs and C_{60}, where the calculated abundance of fullerene was seen to increase and PAH abundance to decrease towards the central star. These observations can be explained by the photo-destruction of PAH and the formation of C_{60}. The possible formation pathway of C_{60} from PAH can be simplified into a few steps. First, the UV photons incident on the PAH initiate dehydrogenation. Once all the H is removed from the edges, it makes graphene sheets. Upon absorption of UV photons, graphene can be fragmented into small flakes. Energy deposited on these small flakes can remove C atoms and minimise the dangling bond energy, so the pentagon starts to appear. This leads to the formation of curvature and, subsequently, a bowl-like structure formed, which are then zipped together and make fullerene. The other proposed structures are small cages, rings, and chains. This proposal was later experimentally verified by Zhen et al.[85] and Berné et al.[79].

Photo-processing of HAC is an alternative pathway for the formation of carbon dust like fullerene. Scott et al.[81] studied the photodecomposition of HAC using the UV laser (308 nm). HAC thin films were grown on the Cu and Al substrates and then irradiated with different fluences (0.09–0.5 J m^{-2}). The gaseous product was analysed using TOF mass spectrometry. This experiment aimed to study the combined effect of thermal, mechanical and photochemical processing of HAC dust. HAC dust can encounter similar energetics under interstellar shock conditions. The analysis of the gaseous product showed the presence of molecular clusters with a wide mass distribution. For low fluence (0.13 J cm^{-2}) irradiation, molecular clusters, including C_{50}, C_{60}, and C_{70}, have been observed, but after exposure to many UV pulses, C_{40} became the most dominant cluster. This indicates the sequential decomposition of HAC, where small molecules and molecular fragments were produced before larger molecular clusters. For high fluence (0.2 J cm^{-2}) irradiation, both low and high-mass molecular clusters were observed even for a single pulse application. After multiple UV pulse applications, the authors claimed the tentative detection of dehydrogenated PAHs such as chrysene (C_{18}), anthracene (C_{14}), and naphthalene (C_{10}) within their gaseous products. Results from these experiments can aid an understanding of the formation of PAH and carbon dust like C_{60} from HAC, decomposed by interstellar shocks.

Destruction of SiC through energetic processing can be another possible route to produce carbon nanodust. SiC has been routinely detected around carbon-rich AGB stars, the second most abundant carbon dust found in presolar grains. However, its spectroscopic detection in the ISM is very rare. The possible reason behind that can be the destruction of SiC grains due to extreme energetic processing. Bernal et al.[84] showed the formation of C_{60} by bombarding energetic ions on the cubic SiC. In vacuum, the SiC particles deposited on a SiN film consist of a microelectromechanical system, which allows the rapid heating of the sample up to 1300 K which may then be bombarded with 150 keV Xe ions. The combination of fast heating followed by ion irradiation mimics ISM shock heating of dust grains. The processed samples were then analysed using scanning transmission electron microscope (STEM), EDX and EELS spectroscopy. From TEM imaging, it was observed that after energetic processing, the SiC crystal had undergone structural modifications. Signatures of graphitization have been found around the edges of SiC crystal. A hemispherical structure with a diameter of around 0.7 nm was observed, which Bernal et al assigned as fullerene. These results can be applied to understand the formation pathways of fullerene in a hydrogen-poor, carbon dust-rich environment like PNe Tc-1.

Recently Bernal et al.[86] have also studied the thermal decomposition of SiC. In this experiment, SiC was initially heated up to 800 ºC with a ramp rate of 25.7 ºC min^{-1}, then heated up to 1500 ºC at a ramp rate of 4.2 ºC min^{-1}, before remaining isothermal for 13 min. In situ TEM observations showed that at temperature ~ 1000 ºC, an increment in the surface graphitization of SiC is observed. In contrast, around 1050 ºC, a hemispherical fullerene-like structure started growing, and multi-walled carbon nanotubes (MWCNT) were detected. It was also noticed that as the isothermal state continued, the MWCNT became much more ordered. To date, the largest carbonaceous molecule known to be present in ISM is fullerene, but this experiment suggests that CNTs can also be a component of interstellar dust.

Merino et al.[83] experimentally investigated the top–down formation pathway of PAHs in a simulated interstellar condition. They exposed graphene terminated cubic SiC surface to atomic hydrogen at an elevated temp ~ 1000 to 1300 K. This led to the erosion of the graphene, and graphene flakes of different sizes were created, which in a hydrogenous atmosphere turned into PAHs.

Pino et al.[87] have experimentally studied the effect of cosmic ray bombardment on the preexisting cosmic carbonaceous dust analogue. The carbonaceous dust analogue was produced from ethylene by burning it in a flame using the same experimental set up previously used by Pino et al.[53] and Carpentier et al.[57]. 4.8 MeV u^{-1} swift heavy $^{48}Ca^{n+}$ ions then irradiated the carbonaceous dust analogue, which was placed at an angle of 45º to the direction of the incident ion beam. The ion matter interaction leaves many ionic and neutral molecular fragments whose mass was recorded using TOFMS technique. Large PAHs with a number of carbon atoms up to 50 and cationic fullerene were detected in the molecular fragments. This experiment suggests that swift heavy ion bombardment on the carbonaceous dust in the ISM can also produce large carbonaceous molecule such as fullerene and PAHs.

4 Synthesis of Cosmic Carbon Dust Analogue Using Shock Tubes

Shock processing of dust in interstellar space can enrich the molecular inventory of the ISM. A detailed discussion of shock waves, and the physical principle of shock tubes and their applications in chemical kinetics can be found in the book by Gaydon and Hurle[88]. In nature, shock waves are created when a perturbation propagates in a fluid medium faster than the speed of sound in that medium. In interstellar space, violent stellar winds can excite and ionise part of the circumstellar medium, creating a rapid pressure gradient to its neutral surroundings creating shock waves. The other sources of shock waves in the ISM are supernova explosions, cloud–cloud collisions, and novae[89,90]. Based on their strength, the interaction of shock waves with the dust gains can give rise to different phenomena such as sputtering, shattering, grain charging, and even direct dust

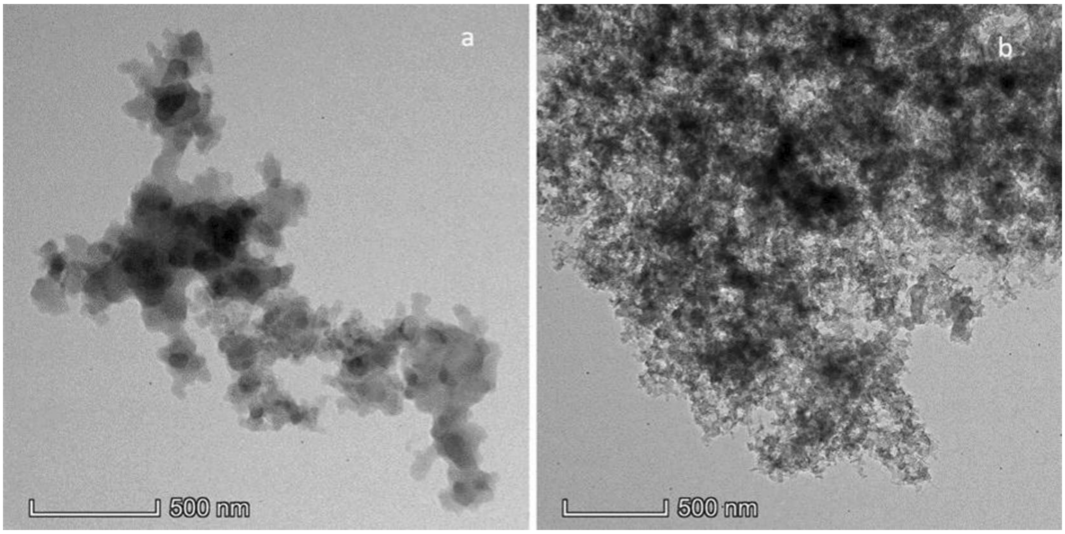

Figure 5: **a** Low-resolution image of the unshocked amorphous carbon nanopowder and **b** is the low-resolution image of the shocked sample, mainly made of sheets.

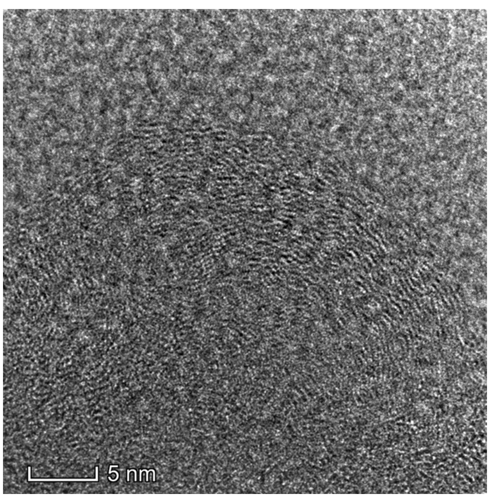

Figure 6: HR-TEM image of the unshocked carbon nanopowder. Random aperiodic orientation of the particles shows that the sample is amorphous in nature.

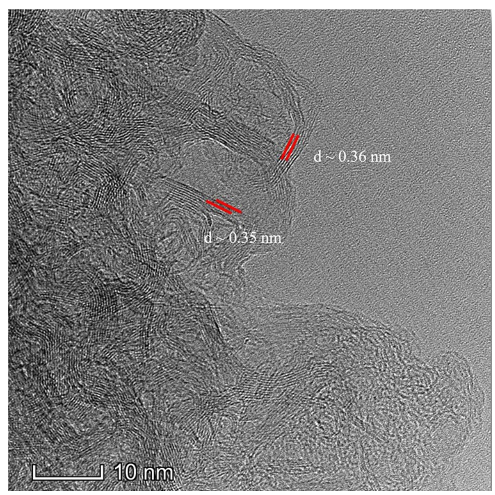

Figure 7: HR-TEM image of the shock-processed sample. It shows the presence of carbon nanoribbons. The interlayer spacing calculated from different parts of carbon nanoribbons indicates that it has a graphitic structure ($d \sim 0.36$ nm). This is a signature of shock-induced graphitization.

grain sublimation[91,92]. Usually, the interstellar shock has a velocity range from 1 to 10^4 km s^{-1}, which can raise the temperature from 10^2 to 10^9 K rapidly[90], whereas high-velocity shock waves are known to be responsible for dust destruction and elemental recycling, collision-induced low-velocity shock (1–2 km s^{-1}) can thermally process the dust making new molecules. These low-velocity shock waves have been detected around many evolved AGB stars[93].

Low-velocity shock waves can be routinely produced in the laboratory using shock tubes. Shock tubes are capable of rapid uniform heating, followed by very fast quenching of the processed materials. This provides an excellent opportunity for the laboratory astrochemist to study the condensation and growth of dust grains from the vapour phase[94,95]. To the best of our knowledge, one of the first experiments devoted to study the formation of SiC from gas-phase precursor using a shock tube was carried out by Carmer and Frenklach[94]. A gaseous mixture of SiH_4, CH_4, H_2 and Ar was shocked in the

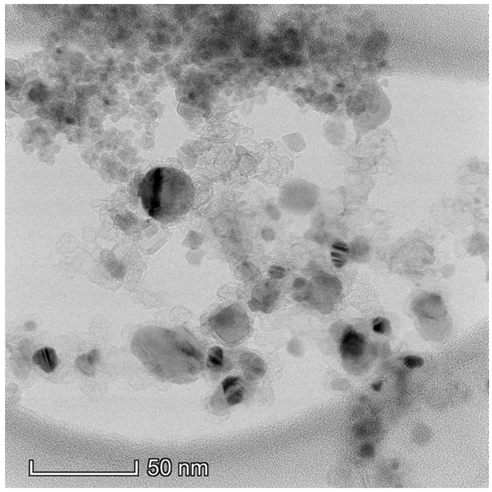

Figure 8: HR-TEM images of the residue produced because of shock processing of ferrocene. Nanoparticles with different shapes and sizes, from spherical particles to nanosheets, are observed.

reflected shock temperature ranging from 800 to 3650 K. TEM analysis of the shock-processed residue showed the presence of Cubic SiC with a particle size of ~20 to 50 nm. No signature of SiC was observed below the reflected shock temperature of 800 K. This experiment showed that SiC formation could be extreme, and its formation rate can be increased with the increase in reflected shock temperature. Its growth rate can be as high as 10^6 µm h^{-1}.

Biennier et al.[96] studied the energetic processing of fullerenes by employing a shock tube. Shock processing of C_{60} in H_2 was investigated up to reflection temperature ~3900 K. The processed solid residues were collected and analysed using XRD, IR, Raman spectroscopy, TEM imaging, and scanning electron microscopy. The gaseous product was analysed using gas chromatography and cavity ring-down spectroscopy. The nature of the solid-state residue is amorphous, with some aliphatic bonds observed. In the gas phase, the detected molecules were CH_4, C_2H_2, C_2H_4, and C_2H_6. Results from this experiment demonstrated the top–down formation of simple hydrocarbon molecules and amorphous carbon dust.

The bottom–up formation route for carbon nanodust demands a high density of precursor materials and high temperature. The top–down formation pathways, on the other hand, are hydrocarbon dependent. Therefore, there is an urgent need to carry out a new set of experiments to understand the possible formation pathways of cosmic carbon dust like fullerene, which has been known to be present in poor hydrocarbon objects such as PNe Tc-1[26] and Lin-49[97]. Our understanding of the evolution of H-deficient amorphous carbon using energetic processing in interstellar space is limited compared to HAC[15,98,99]. H-poor amorphous carbon dust is characterised using their featureless IR continuum emission and is routinely observed around evolved carbon stars[20,100,101]. Shock processing

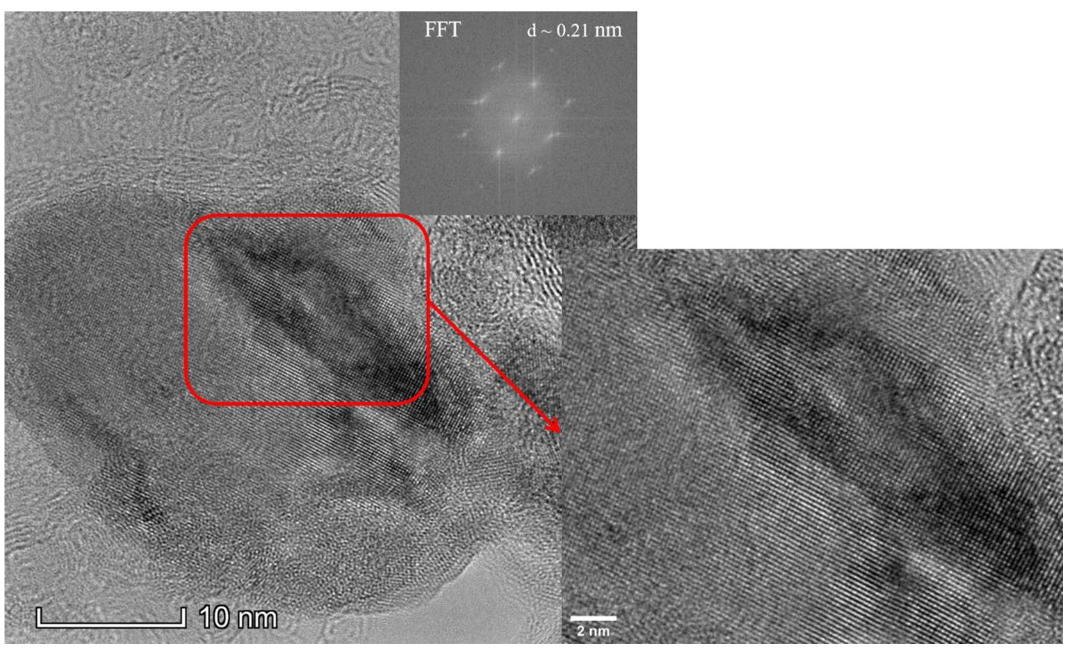

Figure 9: HR-TEM image of iron nano-grains from the shocked ferrocene residue. FFT of the selected area marked by a red rectangle shows that the *d* spacing is around 0.21 nm.

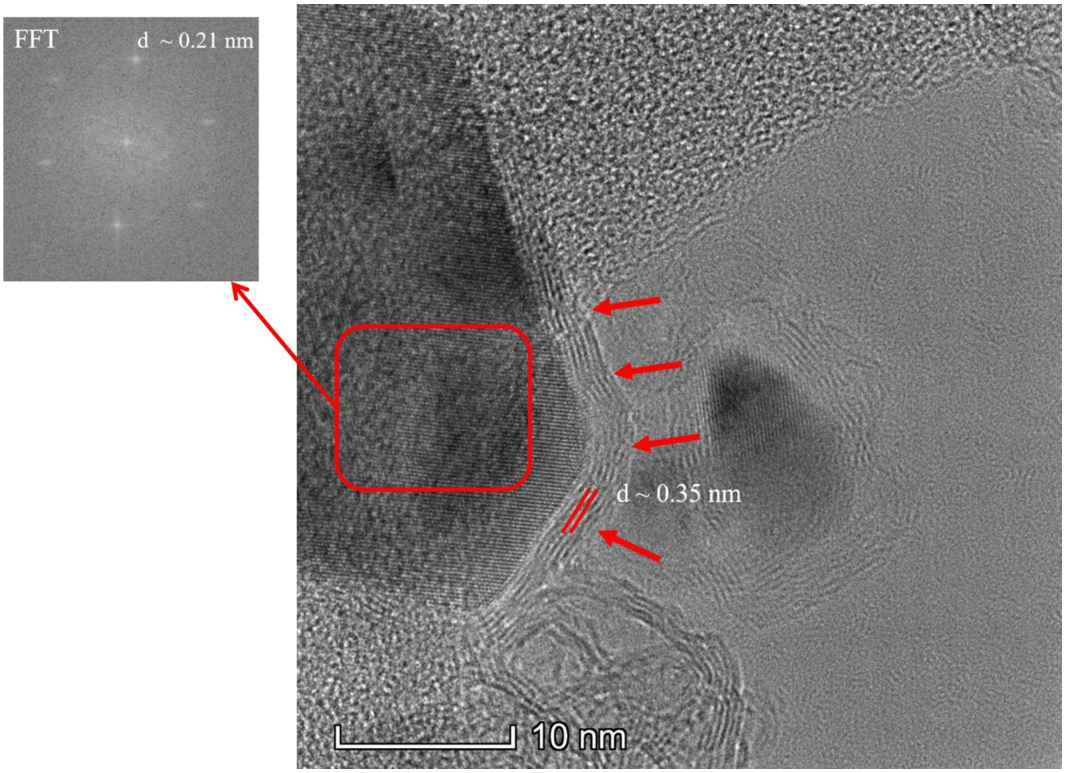

Figure 10: HR-TEM image of the shocked processed residue showing the presence of an iron cluster (*d* ~ 0.21 nm) surrounded by graphitic walls (0.35 nm).

of H-poor amorphous carbon nanodust can be an alternative pathway for the formation of fullerenes in the PNe like Tc-1, where H-poor amorphous carbon is known to be present. Roy et al.[102] have investigated how shocks may induce physicochemical transformation in amorphous carbon by subjecting samples of carbon nano-powder to high-temperature shocks, ~ 7300 K, in a hydrogen-free environment for about 2 ms using a shock tube. The heating rate was as high as 10^6 K s^{-1}, and the quenching rate was around 10^5 K s^{-1}. Post-shock samples were analysed using Raman Spectroscopy and HR-TEM. Different carbon nanostructures were detected, ranging from carbon nanoribbons, nano-onions, nano-cone, carbon nanotube, graphene, graphene quantum dots and fullerene. The most abundant structure was carbon nanoribbons. Raman spectroscopic observation showed that, aftershock processing, the amorphous carbon nanodust has undergone graphitization which might subsequently result in the formation of numerous carbon nanostructures. This experiment showed that fullerene could be made in the ISM via shock processing. Fullerene has been detected in interstellar space, but other carbon nanostructures such as carbon nanoribbons, nano-onions, CNT, graphene and graphene quantum dots can also present as a component of interstellar dust, awaiting discovery. TEM images of both shocked and unshocked samples with different resolutions can be seen in Figs. 5, 6 and 7.

Organometallic molecules are a potential component of interstellar and cometary dust[103]. Recently, cyclopentadiene has been reported in the dark molecular cloud TMC-1. Iron and cyclopentadiene in terrestrial conditions are known to react in the gas phase and make the simplest metallocene molecule, ferrocene. The fate of organometallic molecules subjected to extreme ISM shock conditions is largely unknown. Roy et al.[104] experimentally demonstrated the physio-chemical transformation of ferrocene by subjecting it to the shock waves having Mach ~ 5.6, reflected shock temperature ~ 7300 K within 2 ms. The solid-state residue was analysed using XRD, Raman spectroscopy, IR spectroscopy, HR-TEM, EDX and vibrating sample magnetometer (VSM) technique. XRD of the post-shock residue showed the presence of α-Fe and Fe_3C composite that responded to an external magnetic field. VSM showed that non-magnetic dust composed of molecules containing transition metals undergoing shock processing in the ISM can dissociate and synthesise dust that was then magnetic. Such drastic transformations from non-magnetic to magnetic dust induced by shocks might be of importance in interstellar polarisation. HR-TEM imaging showed the presence of carbon nanoribbons, bare iron clusters and carbon-encapsulated iron nanoparticles. HR-TEM images of the bare iron cluster can be seen in Figs. 8, 9 and 10.

5 Conclusions

We are now entering a new era in which the James Webb Space Telescope (JWST) will revolutionise our understanding of the molecular Universe building upon previous space-borne telescopic missions such as Spitzer and ISO. Utilising these facilities will allow a more detailed exploration of carbonaceous dust. Experiments that have been carried out in the last five years have demonstrated the possibilities of carbon nanostructures such as graphene, graphene quantum dots, CNT, and carbon nanoribbons forming a potential component of cosmic carbon dust, especially in the shock-processed region of the ISM, where only fullerenes are currently known to be present. Our idea of the physical shapes of the dust grains grown on the pre-existing dust surface has changed considerably. The growth of graphene and quantum dots from smaller PAHs in the icy interstellar conditions enrich our idea of bottom–up dust growth, which is considered a practical formation pathway of carbon dust in dense and warm interstellar conditions. However, more experiments need to be carried out, especially the energetic processing of the smaller PAHs which are known to be present in cold, dense molecular clouds. For the high-temperate formation route, the effect of H_2 and other metals such as Fe, Si, and S on carbonaceous dust's structure our knowledge is limited to date. Therefore, more laboratory simulations are needed. The use of shock tubes to study the top–down formation of carbon-containing molecules is developing but as yet is limited to only a few groups worldwide and it is to hoped that more shock tube facilities will be developed to study astronomical phenomena.

Publisher's Note

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Data Availability

The complete set of data will be made available on reasonable request to the corresponding author(s).

Declarations

Conflict of Interest

The authors declared that they do not have any conflict of interest in this work.

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