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Carbonaceous onion-like particles as a component of interstellar dust

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Abstract. The search for the carrier of the 217.5 nm absorption feature in the interstellar extinction curve has been undertaken for the past few decades. We have previously discussed a carbonaceous material named quenched carbonaceous composite (QCC) as a laboratory analog for the interstellar material producing this absorption feature. QCC is condensed from an ejecta of hydrocarbon plasma. High-resolution transmission electron micrographs reveal that QCC is a coagulation of carbonaceous onion-like particles. Each particle consists of multiple shells, and many of the particles have a void at the center. By X-ray photoelectron spectroscopy, the ratio of sp^3-hybridized carbon to sp^2-hybridized carbon in the QCC is estimated to be in the range of 0.16–0.4. This is much lower than other types of materials such as amorphous carbon and hydrogenated amorphous carbon. The 220 nm absorbance peak of the QCC is not stable against heating, suggesting that either a volatile component gives rise to the 220 nm absorption or structural changes occur within the sample. Our experiments indicate that carbonaceous onion-like dust particles are a possible carrier of the 217 nm interstellar medium absorption.

Key words: ultraviolet: galaxies – ISM: dust, extinction – stars: circumstellar matter

1. Introduction

The origin of the 217.5 nm absorption feature appearing in the interstellar extinction curve is a long-standing problem in astrophysics (Draine 1989). Many types of carbon and carbonaceous materials have been proposed to explain the 217 nm feature, including graphite (Stecher & Donn 1965; Draine & Lee 1984), hydrogenated amorphous carbon (HAC) (Duley 1984; Mennella et al. 1995, 1996), coal-like material (Papoular et al. 1996), fullerenes (Krätschmer et al. 1990), graphite onions (Kroto & McKay 1988; Wright 1988; Henrard et al. 1993, 1997, de Heer & Ugarte 1993), diamond-like carbon (Mutschke et al. 1995), a mixture of polycyclic aromatic hydrocarbons (PAHs) (Joblin et al. 1992), and molecular aggregates with aromatic double-ring structures (Beegle et al. 1997). Graphite was first proposed as a candidate for the 217 nm absorption feature in the discovery paper (Stecher 1965). However, the 217 nm absorption maximum of small graphite particles expected theoretically has not been confirmed experimentally. Instead of flat graphite dust, carbon onions (spherical multishell fullerenes) were recently presented as a plausible interstellar graphitic dust by Henrard et al. (1993, 1997) and de Heer & Ugarte (1993).

The carbonaceous materials we used were formed from an ejecta of methane plasma during cooling. A brown-black carbonaceous material named "dark QCC" shows a 220 nm absorption maximum that is very close to that seen in the interstellar medium (Sakata et al. 1983). A yellow-brown filmy material named 'filmy QCC' is collected on a wall surrounding the plasma beam. By thermal treatment at 500–700 C, the filmy QCC is carbonized and shows a 220 nm absorption maximum (Sakata et al. 1994). A soot formed by the combustion of CH_4 and H_2 also shows a 220 nm peak although the peak width is very wide (Sakata et al. 1995).

From these experiments Sakata et al. (1995) suggested that the origin of the 220 nm absorbance peak in the QCC is π electrons in short peripheral carbon chain structures. They also suggested that the hydrogen content in the materials is an important factor in making the conjugated bonds.

Carbon atoms can form three types of bonds with other carbon atoms. The first type is formed from sp^3 hybridization (hereafter sp^3-C), the second type from sp^2 hybridization (hereafter sp^2-C), and the third type from sp hybridization (hereafter sp-C). A π bond and a σ bond (sp^2-C) make a carbon double bond, and two π bonds with a σ bond (sp-C) make a carbon triple bond. π-electrons are the electrons that make these π-bonds.

We report in this paper on the structure of QCC as shown by high-resolution transmission electron microscopy (HRTEM), and we discuss the origin of the 220 nm absorbance peak in QCC. The better resolution of the electron microscope used in the present work provides more details than reported previously by Sakata et al. (1994). We show that QCC is a coagulation of carbonaceous onion-like particles and that each particle consists of multiple shells with defects and with a void at the center. Recent studies of the structure of carbon particles and the results of

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calculated spectra of various onion carbons (Henrard et al. 1993, 1997) indicate the importance of understanding the structure of QCC. We also obtained carbon 1s spectra by X-ray photoelectron spectroscopy (XPS) to provide us with information on the ratio of the sp^2-C and sp^3-C for comparison to other types of carbon materials. Finally, the thermal stability of the 220 nm absorbance peak gives us information about its origin.

2. Experimental procedure

The experimental apparatus for producing QCC was reported by Sakata et al. (1994). QCC is formed from the ejecta of a methane plasma generated by a microwave discharge operating at a frequency of 2.45 GHz. The ejecta left the plasma tube through a narrow hole and were condensed on a room-temperature substrate under vacuum. A brown-black carbonaceous material (dark QCC) formed around the center of the ejecta. We collected the materials on a quartz or a Si crystal substrate. Organic molecules contained in the dark QCC were removed by washing the sample with methanol or with acetone. At the center of the ejecta corresponding to the dark QCC, a black circular spot about 5–7 mm in diameter was formed. Named "granular QCC", it is a high-density condensed carbonaceous material. A third type of carbonaceous material is a yellow-brown organic material (filmy QCC) that was deposited on the wall of the vacuum chamber surrounding the ejecta beam.

In the context of this paper the term "organic molecules" refers to PAH and aliphatic material that is soluble in methanol or acetone. Filmy QCC is composed of such organic molecules. There is also a component of filmy QCC that is mixed with the dark and granular QCC. By washing the dark and granular QCC with methanol and acetone we are removing the filmy QCC component.

We obtained HRTEM images of the dark QCC and the granular QCC with a Hitachi H-9000EM. The QCC samples were mounted on a carbon film supported by a copper microscopic grid. XPS was obtained with a Shimazu ESCA-K1 by irradiation with a Mg K_α source. The spectra were acquired with a 0.1 eV/step energy interval.

For studies of the thermal alteration of QCC, we increased the temperature of the QCC at 5 C per minute and kept it at a given temperature for 20 minutes in a vacuum. After cooling, we measured its UV spectra in air with a double beam spectrophotometer (Hitachi 3000U) with a resolution of 0.5 nm.

3. Result and discussion

3.1. Electron microscopic analysis

In our previous study using transmission electron microscopy (TEM) (Sakata et al. 1994), the QCC materials showed a halo-like diffraction pattern that suggested an amorphous structure. The new images clearly reveal the atomic structure of the QCC and confirm our previous results. One of the authors (C.K.) has used this technique to observe the structure of other materials that had also been thought to be amorphous (Kaito & Shimizu 1984; Kaito et al. 1985).

Fig. 1 shows a TEM image of the granular QCC. Large irregular-shaped masses, each a cluster composed of small particles, can be seen. The electron diffraction pattern and the TEM image of the dark QCC are very similar to those of the granular QCC.

We observed the periphery of the clusters in Fig. 1 by HRTEM, and the images of the granular QCC and the dark QCC are shown in Figs. 2a and 2b, respectively. Onion-like structures exist in both the QCC images. Each particle is composed of concentric shells. The fringe spacing is similar to the (002) lattice spacing of the graphite structure. In the inner part of these clusters, there are complicated structures formed by many onion-like particles clustered together. A HRTEM image of the thermally treated filmy QCC at 500 C also shows that many concentric shell structures are formed in the coagulated material.

The size of onion-like particles in the dark QCC and the granular QCC ranges from 5 to 15 nm in diameter. Larger particles more than 10 nm in diameter are found in the granular QCC. A central vacant core 2–3 nm in diameter is often observed in the particles, as shown at the top of Fig. 2b. Some cores are very round, although most QCC cores are very distorted rather than spherical. We could not observe any clear structure inside the round-shaped core in spite of the 0.18 nm point resolution HRTEM image. In such cases we conclude that the inside of the core is vacant.

The onion-like particles are composed of 3 to 15 concentric shells. Some shells are bent abruptly or are wavy, and in some shells one layer branches into two layers. The interlayer distance for the onion-like particles is not constant, and in some places the interlayer distance is wider than that of graphite (3.34 Å). We surmise that this wider interlayer distance is caused by incorporation of sp^3-C with sp^2-C. Hydrogen atoms and methyl groups might be attached to the sp^3-C. Short curled layers are attached to the surface of the QCC onion. This suggests that the curled layers are the place for the growth of new shells. An onion-like particle consisting of a 2.7 nm core surrounded by nine concentric shells has a diameter of about 9 nm and is composed of about 5×10^4 carbon atoms. For the range of 3 to 15 concentric shells, the number of carbon atoms in the onion-like particle is estimated to be 10^3–10^5.

Carbon onion-like particles, a form of a carbon cluster, were found in the soot produced by an arc discharge between carbon rods (Iijima 1980). They are small particles with a concentric shell structure that are spherical or polyhedral in shape. Ugarte (1992) observed that amorphous carbon changes into quasi-spherical shells under irradiation of an electron beam. He pointed out that spherical structures are favored and planer graphite may not be a stable form in systems of limited size if enough energy is applied. Kuznetsov et al. (1994) found that microdiamonds are changed into carbon onions at high temperature. The evidence therefore suggests that carbon onions are formed under highly energetic conditions as in the case of QCC, which is formed from an energetic plasma. This implies that a large number of atoms must be simultaneously rearranged to form onion shells, though the precise mechanisms are still uncertain even in the case of the single-shell formation of fullerene.

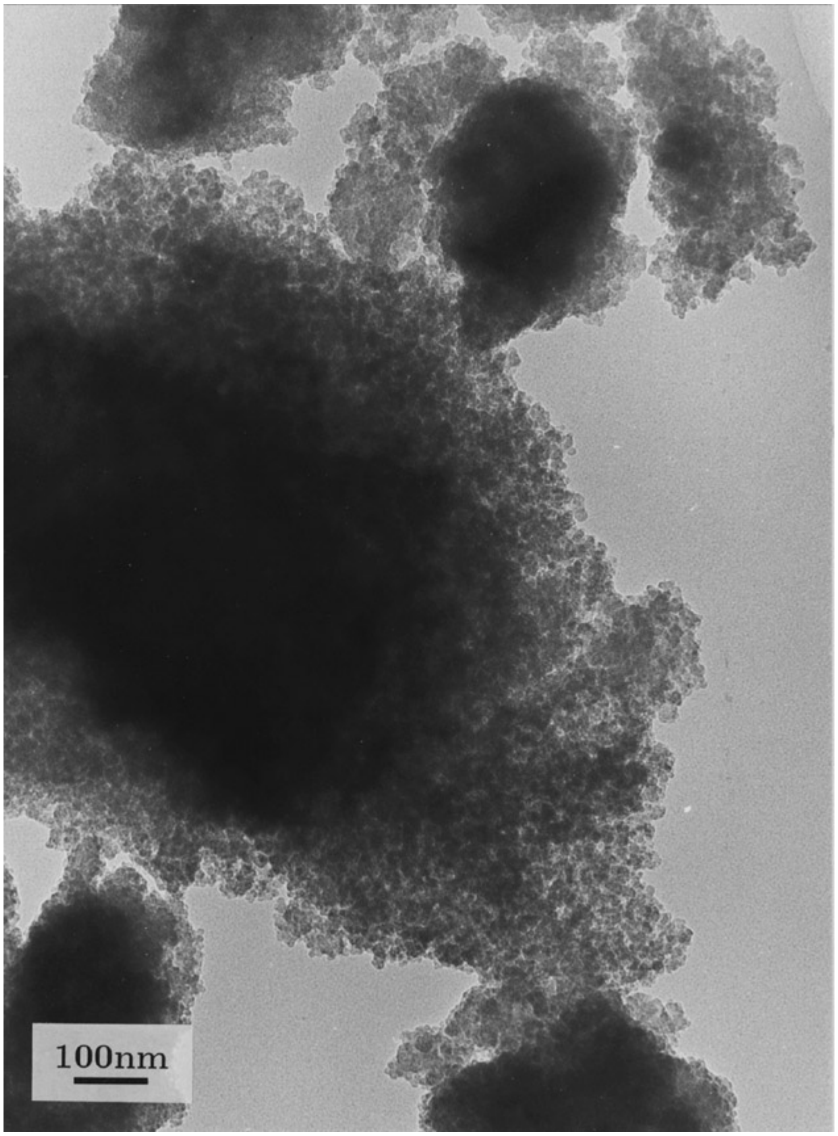

Fig. 1. This TEM image of the granular QCC shows many clusters of small particles.

Characteristic features of the QCC onion-like particles are summarized as follows: (1) Shells are wavy and have many defects, and most of the shells have a central cavity. (2) The core radius is very large compared with the size of the smallest fullerene, C_{60} (7 Å in diameter). (3) Curled small layers are located at the surface. (4) An important difference between QCC and the previously reported carbon onion-like particles is that QCCs are *carbonaceous* onion-like particles composed of carbon and hydrogen, not pure carbon. In the infrared spectra of the dark QCC, and the granular QCC, we have detected bands caused by C–H bonds at 3.3, 3.35, 3.42, 3.49–3.53, 11.4, and 12.0 μm. These bands arise from aromatic and aliphatic C–H bonds.

3.2. X-ray photoelectron spectroscopy (XPS)

XPS provides the energy spectrum of emitted electrons from a solid upon irradiation by soft X-rays. It is plotted as the number of emitted electrons as a function of the electron binding energy. The nature of the chemical bonds of the carbon atoms can be inferred from the spectrum of electrons emitted from the 1s orbital of carbon. Carbon 1s (C1s) spectra of the QCCs are shown in Fig. 3. Compared with the spectrum of graphite, spectra of the dark QCC and the granular QCC are broader on the higher energy side.

Jackson & Nuzzo (1995) studied the sp^3 to sp^2 ratio of carbon materials from the C1s spectra of XPS. Comparing this with the ratio obtained by another method, they concluded that by deconvolution of the C1s spectrum, the amount of hybridization could be obtained. They compared the ratio in amorphous carbon made by the magnetron sputtering and the cathodic arc methods. They found that the peak consists of three components at 284.84, 285.80, and 286.85 eV that correspond to sp^2-C, sp^3-C, and sp^2-C, respectively. In the carbon sample formed by magnetron sputtering, they found that 67.7% was sp^2-C and 32.3% was sp^3-C (sp^3/sp^2=0.48). The carbon sample formed by the cathodic arc method resulted in 33.6% sp^2-C and 66.4% sp^3-C (sp^3/sp^2=2.0). Lascovich et al. (1991) produced hydro-

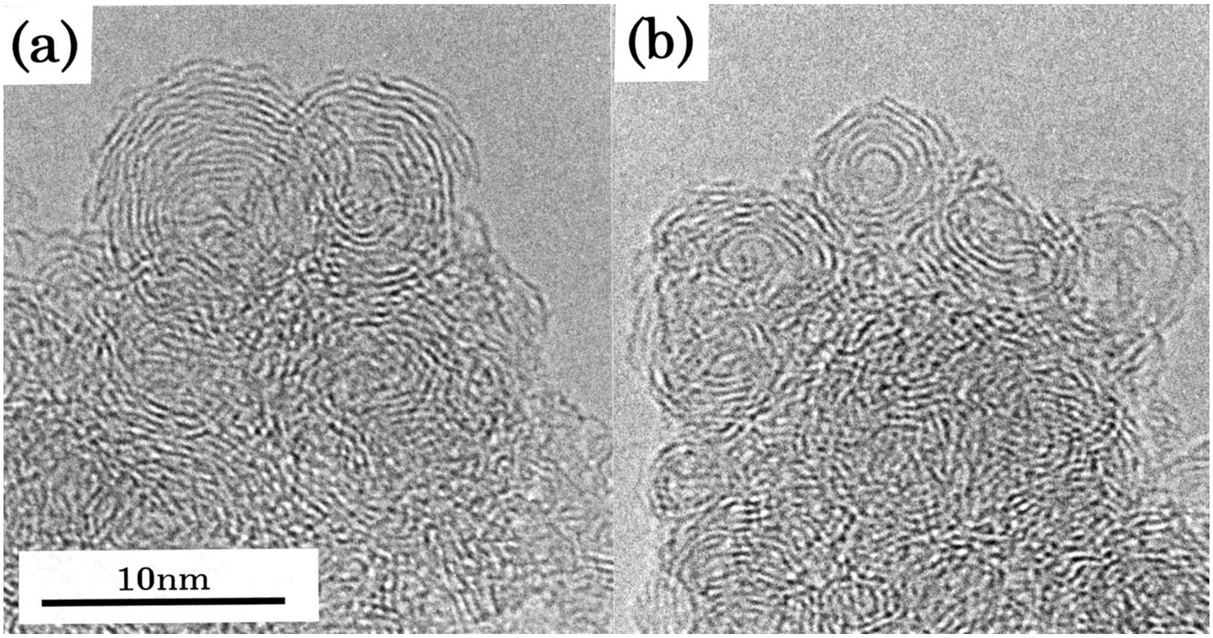

Fig. 2. **a** A HRTEM image of the granular QCC. The material is a coagulation of onion-like particles. The scale of the images of **a** and **b** is shown. **b** A HRTEM image of the dark QCC. The material is also a coagulation of onion-like particles. The particles are a little smaller than those in the granular QCC.

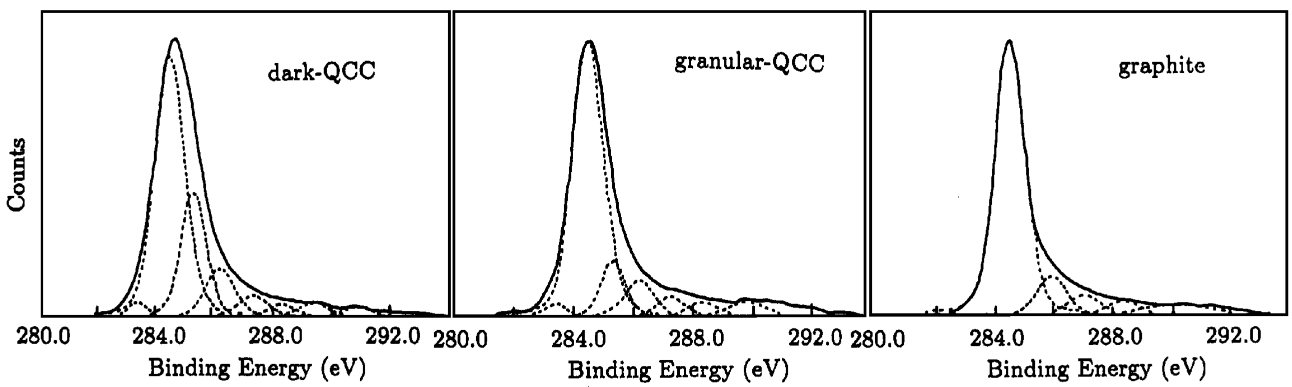

Fig. 3. Carbon 1s X-ray photoelectron spectra (solid lines) of dark QCC, granular QCC, and commercial graphite (T-6, Ibiden Co., Ltd.), and their deconvolved spectra (dotted lines).

genated amorphous carbon samples by the dual ion beam sputtering technique. The percentage of sp^2-C was estimated to be between 20% (sp^3/sp^2=4.0) and 58% (sp^3/sp^2=0.72).

The energy of the peaks is not constant because the sample accumulates charge. In our analysis, the peak of graphite is found at 284.5 eV. After smoothing we fitted the spectra with Gaussian and Lorentzian profiles (Fig. 3). The spectra of the dark QCC and the granular QCC are fitted by curves with peaks at 284.5 and 285.3 eV, which correspond to sp^2-C and sp^3-C, respectively.

We obtained approximate ratios of sp^3-C to sp^2-C in both types of QCC from the areas of peaks at 285.3 and 284.5 eV. The ratios of sp^3/sp^2 are estimated to be 0.16 for the surface of the granular QCC and 0.40 for the surface of dark QCC. Therefore the dark QCC contains more sp^3-C than the granular QCC. Compared with the amorphous carbon and the HACs cited above, both QCCs have high sp^2-C concentration.

The peak found at 286.2 eV and the excess peaks at the higher-energy side indicate that the surface of the granular and dark QCCs is oxidized. Oxidation is confirmed by a small oxygen peak appearing at 533 eV in these samples. Note that our measurements were made without any treatment of the sample, such as surface cleaning with Ar ion bombardment, because such a process would change the carbon bonding substantially (Jackson & Nuzzo 1995).

Oxygen bonded to carbon was also found by infrared absorption spectroscopy of the filmy QCC that was reported previously by Sakata et al. (1987). They found that the absorption band at 6.2 μm was increased, and new bands at 7.7 and 8.6 μm appeared after the QCC sample was exposed to air. These peaks are attributed to a ketone structure with a C=O bond.

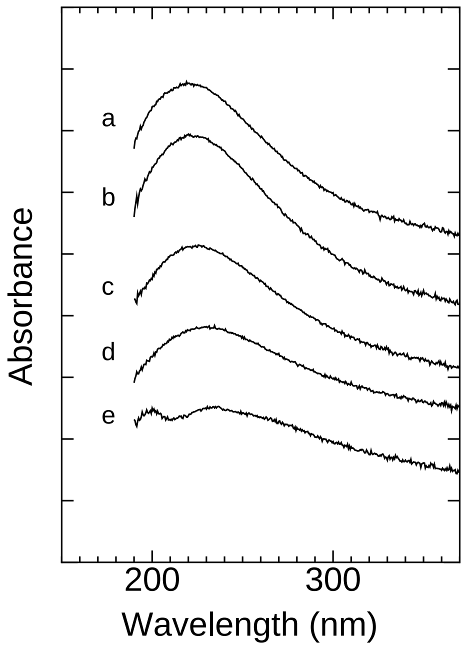

Fig. 4. Spectral change of QCC by heat treatment. The sample and peak wavelength are **a** unheated QCC, 220 nm; **b** after heating at 200 C, 221 nm; **c** after heating at 350 C, 224 nm; **d** after heating at 500 C, 230 nm; and **e** after heating at 700 C, 234 nm (the small peak at 200 nm is often seen).

In summary, XPS shows that QCC contains both sp^3-C and sp^2-C. The granular QCC contains more sp^2 than the dark QCC. Examination by HRTEM shows that larger spherules are more often found in the granular QCC than in the dark QCC. This implies that the inner shells of spherules are composed predominantly of sp^2-C and that most of the sp^3-C is contained in the outer shells of the spherules.

3.3. Thermal treatment

We heated the dark QCC at a given temperature for 20 minutes in a quartz glass container that was evacuated by a rotary pump. After cooling, we measured its UV spectrum in air. The unheated QCC showed an absorbance peak at a wavelength of 217–224 nm. After heating, the absorbance peak was shifted to longer wavelengths. At 700 C the absorbance peak shifted to 233–243 nm. In the range 500 C to 700 C, the loss of volatile material in the QCC occurred. The peak absorbance of the QCC after heating to 700 C was reduced by 75% compared to the unheated QCC. Typical spectra after heating at a given temperature are shown in Fig. 4.

Mennella et al. (1995) heated HAC to study the absorbance peak shift with temperature. Before heating, the HAC does not have any absorbance peak at 200–300 nm. After heating to 450 C, a peak was found at 220 nm, while at 700 C, the peak shifted to 250 nm. These results show that the absorbance peak in the QCC is more stable than that of the HAC upon heating. They interpreted this to mean that the peak shift by heating was caused by growth of the sp^2 cluster.

When QCC is heated, desorption of volatile molecules occurs first. Next the chemical reaction of hydrocarbon components in the solid occurs. Hydrogen attached to carbon atoms is partially removed from the QCC as gaseous products such as CH_4 and C_2H_2. Finally at the highest temperature some structural change of onion-like particles might occur.

The absorbance peak shift occurring in the low temperature range suggests that the origin of the 220 nm absorbance peak has two possible sources. First, it may arise from organic components in the QCC consisting of the material found in filmy QCC. This material remains in the QCC after washing with methanol and acetone and is largely vaporized upon heating. Second, structural change might occur during the heating of the QCC sample and cause shifting of the absorbance peak. In future experiments we will study the structural change during heating with a HRTEM to obtain more information about the origin of the 220 nm absorbance peak in the QCC.

3.4. Discussion

This work was motivated by the close match of the 220 nm absorption feature in QCC to that seen in the interstellar medium. The presence of onion-like particles in QCC is of special interest because recent papers have discussed the possibility of carbon onions in the interstellar medium.

Kroto (1992) suggested that some interstellar carbon particles might consist of concentric graphitic shells surrounded by amorphous outside layers. In addition, Kroto & McKay (1988) suggested that a small amount of hydrogen atoms will perturb the structure, but the hydrogenated shells, which are essentially the same as curled PAHs, are possible carriers of the unidentified infrared emission bands. Using a model of a carbon onion with a central cavity, Henrard et al. (1993) calculated the absorption maximum in the UV region. Their calculation showed that the maximum shifts toward longer wavelengths as the radius of the cavity increases. For a particle outer radius of 7.385 nm, the ratio r/R (the inner and outer radii) of 0.6 reproduced a 220 nm absorption maximum. However, the model requires a narrow range of parameters to match the 220 nm absorption maximum.

Bernatowicz et al. (1991) have found three spherules that have concentric shells of well graphitized carbon and two spherules of poorly graphitized carbon in the Murchison carbonaceous meteorites. The meteorites had anomalous isotopic composition compared to the solar system average, and a TiC crystal was observed in one spherule. As a result they are believed to be interstellar grains. Compared with the QCC onion-like particles, which have a typical diameter of about 10 nm, the sizes of the particles found in meteorites are much larger, and the shell structure is less developed. The meteoritic spherules are very different from QCC and are not likely to be responsible for the interstellar 220 nm hump.

Sakata et al. (1994) suggested two ways a material like QCC might form in the interstellar medium. One is direct formation from the plasmic gas leading to the formation of a material like the dark QCC. The other is a thermal alteration from an organic material like the filmy QCC.

Another possible formation mechanism for such carbonaceous onions is the conversion of precursor carbon dust by processing in the interstellar medium. The conversion of amorphous carbon to carbon onion (Ugarte 1992), carbon onion to diamond (Banhart & Ajayan 1996; Banhart 1997), and microdiamond to carbon onion (Kuznetsov et al. 1994) have been discussed. Henrard et al. (1997) and Ugarte (1995) have also discussed the possibilities of carbon onion formation from microdiamond particles in the interstellar medium.

Heating by shockwave or bombardment by hydrogen ions or atoms, or irradiation by far-ultraviolet radiation will process dust particles in the interstellar medium. Well-ordered carbon onions are not expected to be formed in the ISM. Instead one may expect onion-like carbonaceous spherules with many defects that contain hydrogen and a small amount of oxygen. QCC has absorption bands that are close in wavelength to the 220 nm absorption as well as the infrared emission bands observed in diffuse Galactic emission (Onaka et al. 1996; Mattila et al. 1996). We believe that QCC is similar to the carbonaceous component of the interstellar medium.

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References

Banhart F., 1997, J. Appl. Phys. 81, 3440
Banhart F., Ajayan P.M., 1996, Nat 382, 433
Beegle L.W., Wdowiak T.J., Robinson M.S., et al., 1997, ApJ 487, 976
Bernatowicz T.J., Amari S., Zinner E.K., et al., 1991, ApJ 373, L73
de Heer W.A., Ugarte D., 1993, Chem. Phys. Letters 207, 480
Draine B.T., 1989, On the Interpretation of the λ 2175 Å Feature. In: Allamandola L.J., Tielens A.G.G.M. (eds.) Interstellar Dust. Kluwer, Dordrecht, p. 313
Draine B.T., Lee H.M., 1984, ApJ 285, 89
Duley W.W., 1984, ApJ 287, 694
Henrard L., Lucas A.A., Lambin Ph., 1993, ApJ 406, 92
Henrard L., Lambin Ph., Lucas A.A., 1997, ApJ 487, 719
Iijima S., 1980, Crystal Growth 50, 675
Jackson S.T., Nuzzo R.G., 1995, Appl. Surf. Sci. 90, 195
Joblin C., Léger A., Martin P., 1992, ApJ 393, L79
Kaito C., Shimizu T., 1984, Jpn. J. Appl. Phys. 23, L7
Kaito C., Shimizu T., Nakata Y., et al., 1985, Jpn. J. Appl. Phys. 24, 117
Krätschmer W., Lamb L.D., Fostiropoulos K., et al., 1990, Nat 347, 354
Kroto H.W., 1992, Nat 359, 670
Kroto H.W., McKay K., 1988, Nat 331, 328
Kuznetsov V.L., Chuvilin A.L., Butenko Y.V., et al., 1994, Chem. Phys. Lett. 222, 343
Lascovich J.C., Giorgi R., Scaglione S., 1991, Appl. Surf. Sci. 47, 17
Mattila K., Lemke D., Haikara L.K., et al., 1996, A&A 315, L353
Mennella V., Colangeli L., Blanco, A., et al., 1995, ApJ 444, 288
Mennella V., Colangeli L., Palumbo P., et al., 1996, ApJ 464, L191
Mutschke H., Dorschner J., Henning Th., et al., 1995, ApJ 454, L157
Onaka T., Yamamura I., Tanabé T., et al., 1996, PASJ 48, L59
Papoular R., Conard J., Guillois O., et al., 1996, A&A 315, 222
Sakata A., Wada S., Okutsu Y., et al., 1983, Nat 301, 493
Sakata A., Wada S., Onaka T., Tokunaga A.T., 1987, ApJ 320, L63
Sakata A., Wada, S., Tokunaga, A.T., et al., 1994, ApJ 430, 311
Sakata A., Wada S., Tokunaga A.T., et al., 1995, Planet. Space Sci. 43, 1223
Stecher T.P., 1965, ApJ 142, 1683
Stecher T.P., Donn B., 1965, ApJ 142, 1681
Ugarte D., 1992, Nat 359, 707
Ugarte D., 1995, ApJ 443, L85
Wright E.L., 1988, Nat 336, 227