Ultraviolet-visible absorption spectroscopy of carbon onions

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The optical properties of spherical and polyhedral carbon onions were studied in relation with the strong extinction hump centered at 217.5 nm ($4.6\,\mu m^{-1}$) in the interstellar extinction curve. The ultraviolet-visible absorption spectra of onions prepared by thermal annealing of diamond nanoparticles were measured. Theoretical calculations for the spherical and polyhedral carbon onions were also carried out to explain the experimental spectra.

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The carbon onion is a novel carbon nanoparticle consisting of concentric curved graphene sheets. The physical properties of this new member of fullerene-ralated materials are very much attractive. In particular, the optical properties of carbon onions are of great interest, because they are possible candidates of the interstellar dust, where they could contribute to a strong extinction hump centered at 217.5 nm ($4.6\,\mu m^{-1}$) in the ultraviolet-visible (UV-Vis.) region.

For UV-Vis. absorption properties of the onions, several theoretical analyses have been reported [1,2]. Nevertheless, owing mainly to the small quantity of material available for macroscopic experiments, the absorption properties based on the laboratory experiments remain poorly understood [3].

In 1994, Kuznetsov et al. succeeded in preparing carbon onions in large quantity by annealing diamond nanoparticles about 5 nm in diameter [4]. Such diamond nanoparticles would be synthesized also in the external atmosphere of stars by chemical vapor decomposition of light hydrocarbon molecules; carbon onions are very much likely to be generated in the interstellar space by the transformation of diamond nanoparticles under an appropriate heating process [5]. In relation with this astrophysical context, laboratory data of the UV-Vis. absorption for carbon onions prepared from diamond nanoparticles is highly desired.

Recently, we have prepared spherical and polyhedral carbon onions by annealing diamond nanoparticles in vacuum, and studied them by transmission electron microscopy (TEM), electron energy-loss spectroscopy, Raman spectroscopy, and electron spin resonance (ESR)[6,7]. In the present contribution, we first report the UV-Vis. absorption spectra of these onions. Theoretical calculations for the spherical and polyhedral carbon onions are also carried out to explain the experimental spectra.

1. Experimental results

The detailed sample preparation procedure can be found in elsewhere [7]. Briefly, we prepared carbon onions by annealing diamond nanoparticles 5 nm in diameter in vacuum. As the annealing temperature increases, the transformation of diamond nanoparticles into spherical carbon onions proceeds form the surface to the center [4]. Our previous TEM observation [6] revealed that spherical onions 5 nm in diameter are formed at about 1700°C. At higher temeratures above 1900°C, further progress of graphitization leads to the formation of polyhedral carbon onions with facets [7]. In the present study, diamond nanoparticles were annealed at the temperatures ranging from 900 to 2100°C. The samples were ultrasonically dispersed in distilled water (about 0.2 mg/cc), and then put into a synthesized quarts cell. UV-Vis. transmission spectra in the wavelength ($\lambda\,\mu$m) from 0.5 to $0.2\,\mu$m were recorded with a double-beam type spectrometer. The transmittance (T) was converted into the extinction (E) by using an equation, $E = -\lg T$.

Fig. 1 shows UV-Vis. extinction spectra for all the samples. The horizontal axis is converted into the wavenumber

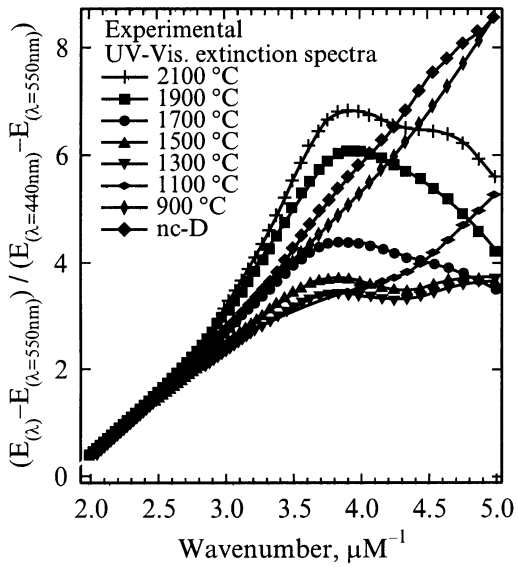

Figure 1. Annealing temperature dependence of normalized UV-Vis. extinction spectra for carbon onions.

$(1/\lambda\,\mu\mathrm{m}^{-1})$. The extinction is normalized by a following equation, $(E_{(\lambda)} - E_{(\lambda=0.55)})/(E_{(\lambda=0.44)} - E_{(\lambda=0.55)})$, where $E_{(\lambda)}$ is the extinction at the wavelength λ. A spectrum for diamond nanoparticles denoted by "nc-D" increases monotonically to the ultraviolet region. The rising extinction continuum cannot be explained by the intrinsic absorption by diamond nanoparticles, and is likely to be caused by the aggregation of diamond nanoparticles. Further discussion on the spectrum for initial diamonds is beyond the scope of this contribution and will be reported in a later papers.

As the annealing temperature increases, the extinction at higher wavenumbers decreases. In addition, the sample annealed at 1100°C shows a broad peak at about $3.8\,\mu\mathrm{m}^{-1}$. At 1700°C, the broad peak is more pronounced and slightly shifted to a higher wavenumber. Note here that spherical onions were observed by TEM at this temperature. With further increasing the annealing temperature, an additional peak at about $4.6\,\mu\mathrm{m}^{-1}$ emerges; a spectrum at 2100°C shows two peaks. The appearance of double peaks is believed to be due to the formation of polyhedral onions.

2. Theoretical considerations

2.1. Spherical onions. A broad extinction hump at $3.8\,\mu\mathrm{m}^{-1}$ observed for the spectra from 1100 to 1700°C is due to spherical carbon onions with diamond or hollow core. The absorption spectra for such onions have already been calculated by Henrard et at. [2]. In their model, by using the spherical coordinates (unit vectors $\bar{\theta}$, $\bar{\phi}$, and $\bar{\rho}$), the dielectric tensor of the graphitic multishell can be expressed as

$$\bar{\bar{\varepsilon}}(\omega) = \varepsilon_{pp}(\omega)(\bar{\theta}\bar{\theta} + \bar{\phi}\bar{\phi}) + \varepsilon_{pl}(\omega)\bar{\rho}\bar{\rho}, \qquad (1)$$

where $\varepsilon_{pp}(\omega)$ and $\varepsilon_{pl}(\omega)$ are the in-plane and out-of-plane dielectric functions of graphite, respectively. The redii of the external graphitic shell and inner core are denoted by R and r, respectively (see inset in Fig. 2). The core, which is filled with diamond or vacuum, is described by an isotropic dielectric function of ε_1. Considering an onion placed in a homogeneous medium with a dielectric function ε_m, the multipolar polarizability of order l is expressed as

$$\alpha(\omega) = 4\pi\varepsilon_0 R^{2l+1} \times \frac{\varepsilon_m[(\varepsilon_{pl}u_- - \varepsilon_1 l)(\varepsilon_{pl}u_+ - \varepsilon_m l) - \rho_l(\varepsilon_{pl}u_+ - \varepsilon_1 l)(\varepsilon_{pl}u_- - \varepsilon_m l)]}{(l\varepsilon_1 - \varepsilon_{pl}u_+)[\varepsilon_{pl}u_- + \varepsilon_m(l+1)]\rho_l - (l\varepsilon_1 - \varepsilon_{pl}u_-)[\varepsilon_{pl}u_+ + \varepsilon_m(l+1)]}, \qquad (2)$$

where $\rho_l = (r/R)^{u_+ - u_-}$, and $u_\pm = -0.5 \pm \sqrt{0.25 + l(l+1)\varepsilon_{pp}/\varepsilon_{pl}}$. At the non-retarded limit, the electric field of a plane-wave electromagnetic radiation with frequency ω only induces an electric dipole $(l+1)$ which absorbs energy from the wave with the cross section

$$\sigma(\omega) = \frac{4\pi\omega}{c}\,\mathrm{Im}\left[\alpha_1(\omega)\right]. \qquad (3)$$

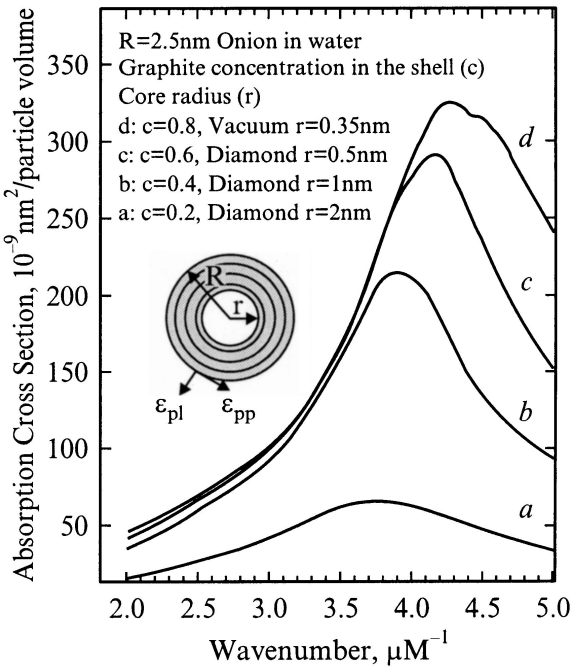

Figure 2. Calculated spectra for the defective spherical onions with external radius $R = 2.5$ nm in water. Inner core radii r are 2 (a), 1 (b), 0.5 (c), and 0.35 nm (d). The cores are filled with diamond for curves a–c, while vacuum for curve d.

Our previous ESR studies for the spherical onions [7] revealed that the graphite shell contains a number of defects such as dangling bonds. The dielectric function of such defective graphite shells should be different from that of bulk graphite. In order to take the effects of defects into our consideration, the dielectric function of defective graphite shells was assumed to be a mixture of those of bulk graphite (ε_{pp} or ε_{pl}) and amorphous carbon (ε_{ac}). The in-plain (ε'_{pp}) and out-of-plain (ε'_{pl}) dielectric functions of defective graphite shell are respectively assumed to be

$$\varepsilon'_{pp} = c\varepsilon_{pp} + (1-c)\varepsilon_{ac}, \quad \varepsilon'_{pl} = c\varepsilon_{pl} + (1-c)\varepsilon_{ac}, \quad (4)$$

where c is the concentration of the graphite component in the shell. We can calculate the absorption cross section of the defective spherical onion from Eq. (1), in which ε_{pp} and ε_{pl} are replaced by ε'_{pp} and ε'_{pl}. In all the calculation, we used the dielectric data of graphite tabulated by Draine and Lee [8], that of diamond by Philipp and Taft [9], and that of amorphous carbon by Michel et al. [10].

Fig. 2 shows the absorption cross section per particle volume (R^3) for several isolated onions. The outer radius (R) is 2.5 nm and the inner radii (r) are 2 (curve a), 1 (curve b), 0.5 (curve c), and 0.35 nm (curve d), respectively. For curve a–c, the inner cores are filled with diamond, while with vacuum for curve d. The surrounding medium was assumed to be water ($\varepsilon_m = 1.777$). The absorption peak due to the surface plasmon in the spherical onion

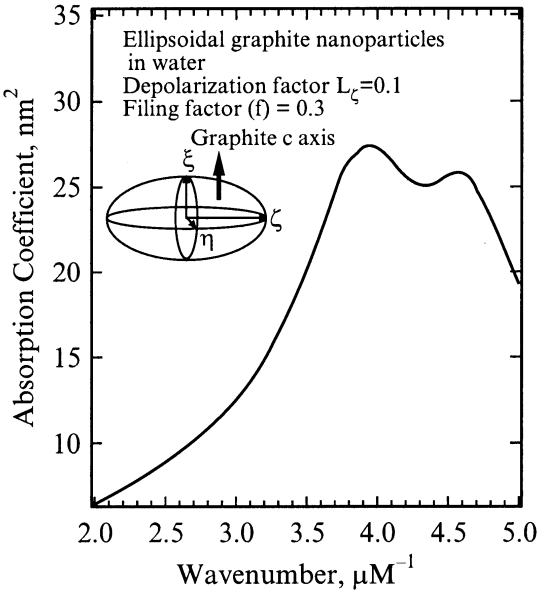

Figure 3. Calculated spectrum for rotational graphite ellipsoids randomly dispersed in water. Depolarization factor $L_\xi = L_\eta = 0.45$, $L_\xi = 0.1$, and filling factor $f = 0.3$.

can be seen at about $3.7\,\mu\mathrm{m}^{-1}$. With increasing c and decreasing r, i.e., as the transformation from a diamond nanoparticle into a defective spherical onion proceeds, the peak shifts to higher wavenumbers. This shift qualitatively agrees with the experimental results. However, the peak of calculated spectra is located at higher wavenumber than that of experimental spectrum. A defective spherical onion without diamond core (curve d) shows the peak at $4.3\,\mu\mathrm{m}^{-1}$, while corresponding experimental spectrum (1700°C) at $3.9\,\mu\mathrm{m}^{-1}$. The wavenumber misfit between calculated and experimental spectra is thought to be caused by the aggregation effect [1]. The aggregation of the onions by van der Waals forces is likely to subsist in water suspension, because the applied ultrasonic dispersion seems to be insufficient to break the adhesion between the particles. The detailed theoretical consideration for the aggregated onions is now underway in our group.

We also simulated an absorption spectrum of a defective spherical onion in vacuum ($\varepsilon_m = 1$). Although not shown here, the calculated spectrum shows a peak at about $4.6\,\mu\mathrm{m}^{-1}$, and just fits the interstellar extinction spectrum. This strongly suggests that a defective spherical onion is a likely candidate for the interstellar dust, which shows an extinction hump centered at $4.6\,\mu\mathrm{m}^{-1}$.

2.2. Polyhedral onions. The appearance of two absorption peaks above 1900°C is apparently attributed to the formation of polyhedral carbon onions with facets. We assume that a polyhedral onion is comprised of planar graphitic nanocrystals, and a nanocrystal can be treated as an anisotropic graphite ellipsoid. Polyhedral onions dispersed in water are thus modeled as a system consisting of anisotropic graphite ellipsoids which are randomly oriented in water. For the discussion of optical properties of the system, we can adopt a framework of average dielectric function for anisotropic ellipsoids developed by Hayashi et at. [11]. For an ellipsoidal particle, ξ, η, and ζ axes are set as shown in the inset in Fig. 3. Dielectric functions along each axis are expressed by ε_ξ, ε_η, and ε_ξ. Introducing depolarization factors (L_j $j = \xi, \eta, \zeta$) along j axis and a filling factor (f), the average dielectric function can be written as

$$\varepsilon_{\mathrm{av}} = 1 + \frac{3(1-f)(\varepsilon_m - 1) + f(\tilde{\varepsilon}_\xi + \tilde{\varepsilon}_\eta + \tilde{\varepsilon}_\zeta)}{3(1-f) + f(\hat{\varepsilon}_\xi + \hat{\varepsilon}_\eta + \hat{\varepsilon}_\zeta)}, \qquad (5)$$

where

$$\hat{\varepsilon}_j = \left[1 + L_j\left(\frac{\varepsilon_j}{\varepsilon_m} - 1\right)\right]^{-1}, \quad j = \xi, \eta, \zeta, \qquad (6)$$

$$\sum_j L_j = 1, \qquad (7)$$

$$\tilde{\varepsilon}_j = (\varepsilon_j - 1)\hat{\varepsilon}_j, \quad j = \xi, \eta, \zeta. \qquad (8)$$

Here the absorption coefficient is directly given by

$$\alpha = \frac{4\pi\omega}{c}\,\mathrm{Im}\,\sqrt{\varepsilon_{\mathrm{av}}}. \qquad (9)$$

In the present study, ξ axis of the ellipsoid is set parallel to the graphite c axis. Therefore, ε_ξ corresponds to ε_{pl}, while ε_η and ε_ζ to ε_{pp}. For depolarization factors, by assuming a rotational ellipsoid, we set $L_\xi = L_\eta$, and $2L_\xi + L_\zeta = 1$. Fig. 3 shows a calculated absorption coefficient for the graphite ellipsoid in water. L_ξ is 0.1, L_η and L_ζ are 0.45, and f is 0.3. The graphite ellipsoids that we considered here successfully reproduce an absorption spectrum with two peaks. These two absorption peaks at about 4.0 and $4.6\,\mu\mathrm{m}^{-1}$ are induced by surface plasmons along η and ξ axes of ellipsoid.

We have studied the optical properties of spherical and polyhedral carbon onions in relation with the interstellar dust particles. The laboratory absorption spectroscopy indicated that spherical onions in water show a broad extinction peak at about $3.8\,\mu\mathrm{m}^{-1}$. The theoretical calculation suggested that the peak is due to the surface plasmon in the defective spherical onion. Furthermore, the calculated spectrum for the defective onion in vacuum can reproduce the interstellar extinction spectrum. This suggests that the defective spherical onion is a strong candidate for the interstellar dust, which shows an extinction hump centered at $4.6\,\mu\mathrm{m}^{-1}$. Experimental spectra for polyhedral onions showed two extinction peaks at 3.9 and $4.6\,\mu\mathrm{m}^{-1}$. Approximating the facet of the polyhedral onion as a graphite ellipsoid and applying a framework of the average dielectric function, we succeeded in reproducing the absorption spectrum with double peaks. Both peaks originate from the surface plasmons in the facet part of the polyhedral onion.

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