



Characterisation of carbon nano-onions using Raman spectroscopy

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Abstract

Characteristics of the Raman spectrum from carbon onions have been identified in terms of the position of the G peak and appearance of the transverse optic phonon peaks. Five new peaks were observed in the low wavenumber region, at about 1100, 861, 700, 450 and 250 cm^{-1} . The origins of these peaks are discussed in terms of the phonon density of states (PDOS) and phonon dispersion curves of graphite. The curvature of the graphene planes is invoked to explain the relaxation of the Raman selection rules and the appearance of the new peaks. The Raman spectrum of carbon onions is compared with that of highly oriented pyrolytic graphite (HOPG). The strain of graphene planes due to curvature has been estimated analytically and is used to account for the downward shift of the G peak.

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1. Introduction

Since the discovery of fullerenes [1] and carbon nanotubes [2], there have been intensive efforts to produce and characterise nano-structured carbon materials, with the main objective being to exploit their properties for electronic and mechanical applications. Examples of nano-structured carbon include nanotubes, nano-onions and nano-cones. Transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), Raman spectroscopy and scanning electron microscopy (SEM) are generally used to characterise these structures.

Of these, Raman spectroscopy is the most useful non-destructive technique capable of differentiating between these various structures [3–7]. Raman spectra of diamond [4,8], graphite [3,7] and carbon nanotubes [5,9] are well understood. However, there are very few reports on Raman spectroscopy of carbon nano-onions [6,10], with no report hitherto of Raman features specific to carbon nano-onions. In this Letter, characteristics of Raman spectra from carbon nano-onions are reported.

2. Experimental procedures

The nano-onions used in this work were produced by applying a DC voltage across two

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graphite electrodes submerged in water, generating an arc discharge between them [11]. The discharge current and voltage were 30 A and 16–17 V, respectively. The nano-onions were mostly found floating on the surface of the water. TEM investigation was performed with a JEOL 4000 EX transmission electron microscope operated at 400 kV. The TEM specimen was prepared by dipping the holey carbon grid into the water and scooping out the onions from the surface. Raman measurements were taken with three different wave length of laser (514.5, 633, 785 nm) using a Renishaw Raman microscope (Model-1000), covering the spectral range of 200–1800 cm^{-1} .

3. Results

A TEM micrograph of the carbon nano-onions is shown in Fig. 1. The diameter of the onions was found to range from 5 to 50 nm [11]. In some well-crystallized onions, the diameters of the innermost

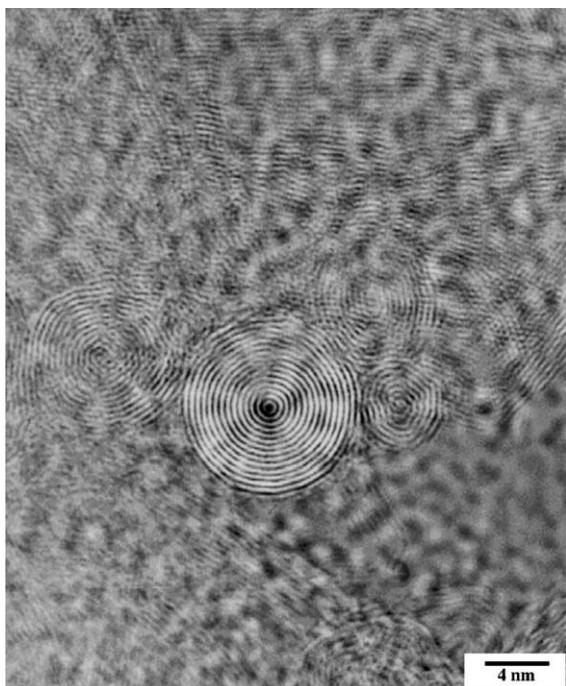


Fig. 1. High-resolution transmission electron micrograph of carbon onions.

cores were found to be ~ 0.7 – 0.8 nm, consistent with the diameter of the C_{60} molecule. Two types of onions were found in our samples. The first type is well-crystallized onions with diameter in 5–20 nm range and the second were larger onions which were poorly crystallized [11]. In addition to the onions in Fig. 1, disordered carbon from the holey carbon TEM grid can also be seen. The phonon dispersion curves and the phonon density of states (PDOS) of 2D graphite are shown in Figs. 2 and 3a,b respectively. Raman spectra from nano-onions are shown in Fig. 3c–h, and from highly oriented pyrolytic graphite (HOPG) in Fig. 3i,j. Weak D peaks along with sharp G peaks in the Raman spectra (Fig. 3c–h) clearly indicate high purity of carbon onions in the sample. However, it is very difficult to provide a quantitative estimation of the purity from the relative intensities of the D and the G peak or the TEM images. It should be noted that the Raman spectrum of the electrode material showed a large D peak (not shown) consistent with polycrystalline crystalline graphite. As with the spectrum of graphite [3] (see Fig. 3i), a sharp G peak is apparent (see Fig. 3c,e,g). The G peak width is considered to be a qualitative measure of the quality of graphene planes. A G peak, only slightly wider than that of HOPG (the FWHM is

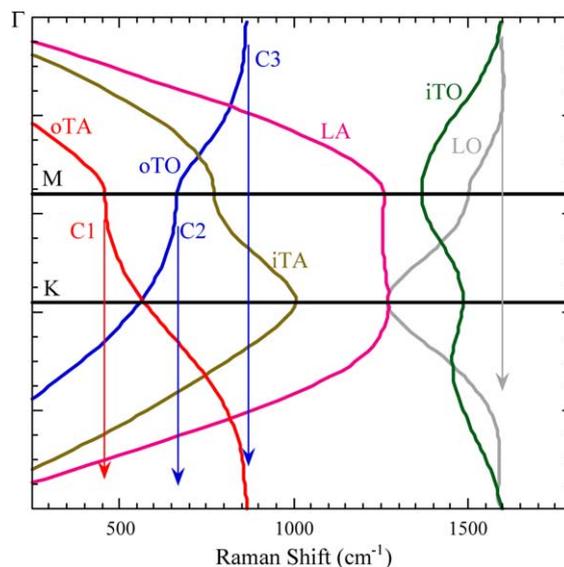


Fig. 2. Dispersion curve of 2D graphite, after Lespade et al. [7].

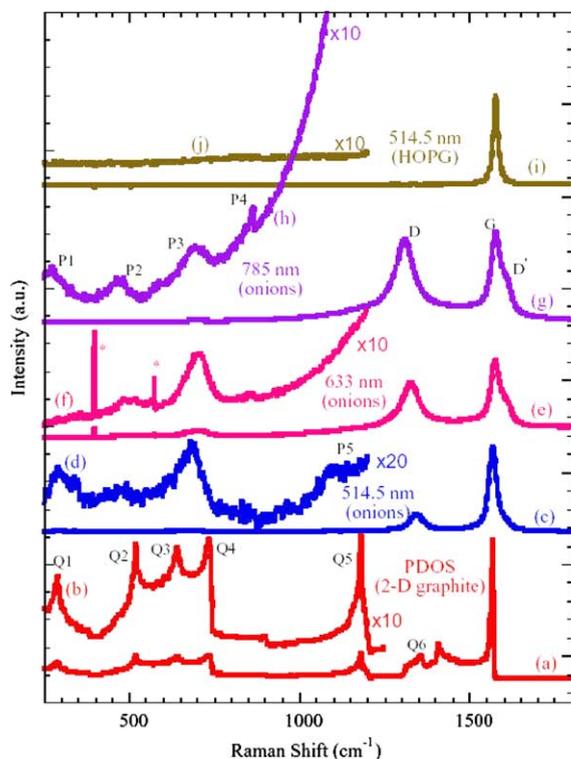


Fig. 3. (a) Phonon density of states (PDOS) of 2D graphite, after Lespade et al. [7]; (b) part of PDOS spectrum, magnified by a factor of 10; (c) 514.5 nm Raman spectrum from onions; (d) part of 514.5 nm onions spectrum, magnified by a factor of 20; (e) 633 nm Raman spectrum from onions; (f) part of 633 nm onions spectrum, magnified by a factor of 10; (g) 785 nm Raman spectrum from onions; (h) part of 785 nm onions spectrum, magnified by a factor of 10; (i) 514.5 nm Raman spectrum from HOPG and (j) part of the 514.5 nm spectrum of HOPG, magnified by a factor of 10.

25 cm^{-1} for the onions (Fig. 3c), compared with 15 cm^{-1} for the HOPG (Fig. 3i)) signifies a high degree of perfection in the graphene planes in the onions.

It can be seen that the G peak centre of the onions has been shifted downward slightly ($1569\text{--}1577 \text{ cm}^{-1}$ at various locations), compared to that of HOPG (1582 cm^{-1}). A similar downward shift has also been observed by Obraztsova et al. [6] and Bacsá et al. [10]. It seems likely that it is due to tensile strain in the graphene planes, induced by the curvature. When a graphene plane, having hexagonal blocks of atoms, is deformed into a spherical shape by introducing pentagons (from

Euler's theorem for polyhedra there can be 12 pentagons and arbitrary number of hexagons in a shell depending on its diameter) [12], the bond lengths increase depending on their position on the sphere, so that tensile strain is induced in the lattice. Considering an average bond stretching due to this curvature, the average bond length (a') can be estimated as a function of onion diameter from the expression

$$a' = a \sqrt{\left(1 + \frac{a^2}{4R^2}\right)}. \quad (1)$$

The average strain (ε) in the lattice is given by

$$\varepsilon = \frac{(a' - a)}{a}. \quad (2)$$

The average strain in the lattice can be expressed as

$$\varepsilon = \sqrt{\left(1 + \frac{a^2}{4R^2}\right)} - 1, \quad (3)$$

where a' is the average C–C bond length in a shell of radius R and a is the C–C bond length in planar graphene sheet (0.142 nm). For example, for C_{60} ($R = 0.36 \text{ nm}$, observed C–C bond length is 0.144 nm) [12], the calculated bond distance a' (using Eq. (1)) is 0.1448 nm . As expected, smaller onion diameters lead to larger strains. This simplified model neglects the strain accommodated due to incorporation of the pentagons, which accounts for the slight overestimation in case of small molecules such as C_{60} . Another limitation of the model is that it estimates the average strain in the hexagons only (which indeed outnumbers the number of pentagons in case of a shell of larger diameter).

Another strong peak appears at 1344 cm^{-1} (Fig. 3c,e,g). It is a disorder-induced peak (D peak [3,13]). It may be noted that no D peak is observed in the Raman spectrum of HOPG, which is defect-free. In the dispersion curve of graphite (Fig. 2), there is no Raman-active phonon at the Γ point near 1350 cm^{-1} . Therefore, no D peak is observed with HOPG (Fig. 3i). The difference in the relative intensities of the D peak, for different laser wavelengths, is attributed to resonance at different energies. Double resonance has been invoked to

explain the appearance of the D peak from disordered graphites [13,14]. The ratio of the intensities of D and G peaks is often used to estimate the degree of perfection of graphene planes [3]. For example, the absence of the D peak with HOPG implies perfect graphene planes. Thus, a very weak D peak and a strong G peak from carbon nano-onions signify that only slight imperfections are present in the graphene planes of the onions. Along with the G peak, another weak band is observed near 1600 cm^{-1} , which is assigned as a D' peak (Fig. 3c,e,g). It is also a disorder-induced peak [15] and thus not observed in HOPG, but often observed in highly-defective graphite. It appears to be due to scattering from the LO phonon branch, away from the Γ point. It is clear from the presence of the D and D' peaks that there is some disorder in these carbon nano-onions. The D and D' peaks may also be attributed to the presence of amorphous carbon which is also present in the sample.

Although D and G peaks are strong features of the Raman spectrum of carbon nano-onions, and match well with those of graphite, some Raman peaks can also be observed in the low/intermediate wavenumber region of the spectrum. Carbon onions show broad peaks near 250 cm^{-1} (P1), 450 cm^{-1} (P2), 700 cm^{-1} (P3), 861 cm^{-1} (P4) (Fig. 3h) and 1200 cm^{-1} (P5) (Fig. 3d), but these are absent in the HOPG spectrum (Fig. 3j). P1, P2, P3 and P4 peaks can also be observed with the other laser wavelengths (Fig. 3d,f). However, their relative intensities are different. The P5 peak which is observed with the 514.5 nm laser (Fig. 3d) may be masked by the D peak in Fig. 3f,h. None of these peaks have been reported previously from carbon onions. Relaxation of the Raman selection rule, due to curvature of the graphene planes in the shells, is presumed to be the cause of the appearance of the new bands. Similar low/intermediate wave number peaks have also been reported by Tan et al. [16] from graphite whiskers.

The peaks observed in Fig. 3c–h can be correlated with the 2D PDOS of graphite (Fig. 3a,b) and with the phonon dispersion curves (Fig. 2). The position of the P1 peak ($\sim 280\text{ cm}^{-1}$, Fig. 3h) matches well with Q1 in Fig. 3b. No such obvious correspondence could be found for the peaks P2,

P3 and P4. However, the wavenumbers of peaks P2 ($\sim 450\text{ cm}^{-1}$) and P3 ($\sim 670\text{ cm}^{-1}$) match well with points C1 and C2 in Fig. 2, i.e., the M points on the out-of-plane transverse optic (oTO) curve and on the out-of-plane transverse acoustic (oTA) curve. Therefore, the M point zone boundary phonon mode, with out-of-plane vibrations (oTO and oTA), is a possible source [17,18] of the P2 and P3 peaks. The wavenumber of the P4 peak ($\sim 870\text{ cm}^{-1}$) matches well with the oTO phonon near the Γ point (point C3 in Fig. 3). It may also be noted that this peak is absent with 633 and 785 nm lasers. The origin of the P5 peak is not yet clear, but the Q5 peak in the PDOS (Fig. 3b) may be responsible.

Graphene planes exhibit pronounced curvature in various carbonaceous materials [11,16,19–21]. This seems to be particularly common in the presence of N, which may become incorporated into the planes and reduce the energy penalty associated with pentagonal ring structures. In these nano-onions, there is no N present, but the curvature is pronounced and systematic. Various explanations have been put forward [19,22–24] concerning features of Raman spectra observed in the presence of N, although none of these have related to curvature of the graphene planes.

4. Conclusions

In summary, new Raman peaks have been observed with carbon nano-onions and their possible origins have been discussed in terms of 2D PDOS and dispersion curves of graphite. The M point zone centre phonons of the oTO branch give rise to peaks at 450 and 700 cm^{-1} , and the 861 cm^{-1} peak arises from the oTO branch at the Γ point. The peaks at 250 and 1100 cm^{-1} are explained in terms of the maxima in the PDOS of graphite at those positions. The perfection of the graphene planes is qualitatively deduced from the weak D peak and strong G peak. Tensile strain in the curved graphene planes is proposed as being at least partly responsible for the observed downward shift of the G peak. A calculation of the bond length distortion has been performed, to determine the tensile strain in the graphene planes

induced by curvature. Therefore, a strong G peak with a wavenumber below that of HOPG, and certain intermediate wave number peaks, both appear to be characteristic features of the Raman spectrum of carbon onions.

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