Diameter dependence of interwall separation and strain in multiwalled carbon nanotubes probed by X-ray diffraction and Raman scattering studies

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A B S T R A C T

We have made a systematic study on the diameter dependent spectral features in X-ray diffraction (XRD) and Raman scattering studies of multiwalled carbon nanotubes (MWCNTs) of various diameters in the range 5−100 nm. High resolution transmission electron microscopy (HRTEM) imaging reveals a systematic decrease in the interwall separation from 3.8 Å down to 3.2 Å as the diameter of nanotubes increases from 5.8 nm to 63.2 nm. Analysis of the XRD patterns shows an exponential decrease in d002 interlayer spacing with increasing tube diameter, in close agreement with the HRTEM results. Further, XRD profile line width shows inverse diameter dependence and exponential increase in intensity as the diameter of the MWCNTs increases. Raman spectra of different diameter nanotubes show different evolutions of metallic and semiconducting components in the G-band, as found from spectral deconvolution. The frequency and full width at half maximum (FWHM) of the semiconducting component of the G band gradually decreases as the tube diameter increases. Ratio of intensities of G’ band to D-band first shows a sharp fall as the tube diameter increases from 7 nm to 15 nm and then slowly increases with increasing diameter. On the other hand, G’ mode frequency shows large up shift when average diameter is increased from 7 nm to 15 nm and then saturates for higher diameter tubes. Analysis of Raman and XRD data reveals that the lowest diameter (7 nm) MWCNTs have features similar to those of the single walled nanotubes, while the spectral features are distinctly different for higher diameter MWCNTs due to the interaction among tube walls that is very significant for large diameter MWCNTs. Observed diameter dependence of the spectral features is explained in terms of nanotube curvature and atomic vibrations involving interaction among the walls in MWCNTs. The present study demonstrates the power of XRD for nondestructive evaluation of diameter distribution and interwall separation in MWCNTs with wide range of diameters.

1. Introduction

Since their discovery, the single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) have prompted numerous studies of their structure, properties and potential applications. MWCNTs offer remarkable electrical, mechanical and chemical properties similar to SWCNTs with less cost and comparatively lesser carbonaceous and metallic impurities. In spite of numerous applications demonstrated using MWCNTs, no protocol exists for characterizing and quantifying these materials. Protocol [1] and various experimental methods [2] of characterization of SWCNTs have been well studied. Diameter dependent optical properties of SWCNTs have been extensively studied [3]. Raman spectroscopy has evolved as a tool to probe the properties of carbon nanotubes like diameter distribution, chirality, doping, nature like semiconducting or metallic, etc [4]. Detailed analysis of mean diameter and diameter distribution of SWCNTs has been done from their optical response [5]. Diameter grouping of bulk samples of SWCNTs from optical absorption spectroscopy has been illustrated [6]. Raman scattering intensity is known to depend on the diameter for SWCNTs [7]. But most of optical spectroscopy techniques cannot be applied directly to MWCNTs due to multiple absorptions and emission between concentric cylindrical structures. Resonance effects and small penetration depth of visible lasers into nanotubes may limit the use of Raman spectroscopy for quantitative characterization of macroscopic volume of MWCNTs. X-ray diffractometry (XRD) is a nondestructive method of characterization revealing information about the interlayer spacing, the structural strain and the impurities. However diameter and chirality distribution in carbon nanotube samples make multiple orientations with respect to the X-ray beam leading to a statistical result. XRD probes milligram of sample without any specific selection between carbon nanotubes in the sample. Diffraction profile resulting from X-ray scattering has been used to characterize double walled carbon nanotubes (DWCNTs) [8]. XRD has been recently demonstrated to be useful for the characterization of...
composition and structure of macroscopic amount of DWCNTs [9]. Temperature dependent XRD has been used to distinguish between the Russian doll and jellyroll type structures of MWCNTs [10]. Theoretical studies of XRD patterns of graphite and turbostratic carbon have shown that increase in the curvature of the graphite sheet leads to increase in the Bragg angle and decrease in the FWHM [11]. Contribution of particle size broadening and strain broadening resulting from distribution of d-spacing has been estimated from powder XRD profiles for carbon nanotubes. It was observed that the major contribution to the width of the (001) peak arises from strain rather than finite size effects [12]. Early studies on carbon nanotubes and nanocapsules using XRD and electron diffraction have shown that the interlayer spacing between layers of carbon nanotubes is about 2.6% higher than the graphite [13]. Structure of carbon nanotubes including the nature of disorder has been studied using computed and experimental XRD data [14]. XRD has been used to characterize the degree of alignment in as-grown nanotubes [15]. However, no systematic studies are reported on the diameter dependence of the XRD pattern of MWCNTs. Further, the properties of large diameter nanotubes in the diameter range 10–100 nm are least explored in the literature. Majority of the reported studies have been carried out on MWCNTs of diameter up to 10–15 nm.

In the literature, only a few of the studies are dedicated to Raman spectroscopic analysis of MWCNTs. RIBM like feature in MWCNTs is reported to originate from the innermost wall of MWCNTs and it is found to be inversely proportional to the diameter of the innermost tube [16,17]. It has been proposed that the inner tubes of a MWCNT contribute to the SWCNT-like feature in the spectra, while the other tubes more closely resembled graphite [18]. Splitting of graphitic mode C-band has been observed in case of MWCNTs [17]. High resolution transmission electron microscopy (HRTEM) has been utilized to find the interlayer d-spacing that showed an increase in the d-spacing with decreasing diameter of MWCNTs having diameter less than 10 nm [19]. However, large diameter MWCNTs with diameter in the range of 10–100 nm have not been studied systematically. A recent study has shown influence of diameter of MWCNTs on the Raman shift [20]. However, no detailed analysis was made on the diameter dependence of line width, intensity and splitting of G-band in Raman spectra [17]. In this work, we have studied the diameter dependence of interwall separation and strain in MWCNTs of a wide range of diameters (5–100 nm) using XRD and Raman scattering studies. The results are corroborated by HRTEM analysis. Origin of diameter dependence is discussed in light of the experimental results.

2. Experimental details

MWCNTs used in this work were grown by catalytic chemical vapor deposition using metal catalysts and subsequent acid purification and these were procured from Shenzhen Nanotech, China. These MWCNTs are 5–15 μm long and of six diameter ranges: <10 nm, 10–20 nm, 10–30 nm, 20–40 nm, 40–60 nm and 60–100 nm that have been studied systematically to identify the features related to the average diameter of the nanotubes. The samples are named as per the average diameter found from HRTEM imaging, which was found to be quite consistent with the mean diameter specified by the supplier. For example, sampleCNT-7 indicates an average diameter of ~7 nm for the lowest diameter (<10 nm) MWCNTs. Details of the samples with nomenclature are provided in Table 1. High resolution powder XRD spectra were recorded in para-focusing geometry of the Bragg–Brentano optics using lock coupled scan mode with Cu-Kα line (Bruker, D8 Advanced). Raman spectra were recorded in the backscattering mode using 488 nm Ar laser and CCD detector coupled to a high resolution monochromator (Jovin Yvon, Triax 550). Structure and morphology of the MWCNTs were studied using a 200 keV high resolution TEM (JOEL 2010). Gatan DigitalMicrograph software was used to process and analyze the HRTEM images.

3. Results and discussion

3.1. HRTEM studies

HRTEM imaging is utilized to measure the actual diameter distribution and interlayer spacing in the MWCNTs. Fig. 1 shows HRTEM images of various diameter MWCNTs studied including the high resolution lattice images of different diameter MWCNTs. Fig. 1(a–f) shows the morphological and diameter distribution of MWCNTs as observed under the microscope. The average diameter of a sample was estimated by taking the average of 20 nanotubes for each sample seen under HRTEM imaging. HRTEM studies show that the smallest diameter (<10 nm) sample has an average diameter of ~7 nm and the higher diameter tubes have an average diameter close to the mean value of the diameter specified by the supplier. For example, the sample with a diameter range of 20–40 nm has an average diameter of 30.5 nm, as shown in Fig 1(c). HRTEM images shown in Fig. 1(g–k) show that the interplanar spacing d002 varies with the diameter of MWCNTs. We have observed a systematic and significant reduction in d002 spacing from 3.8 Å to ~3.2 Å as the diameter increases from 5.8 nm (CNT-7) to 63.2 nm (CNT-50) shown in Fig. 1(l). It is also evident that as the diameter of the MWCNTs increases the number of coaxial cylindrical layers increases. Earlier studies using HRTEM showed that interplanar spacing decreases exponentially and approaches 3.4 Å lattice spacing of turbostratic graphite as the diameter of the MWCNTs increases to 10 nm [19]. Interplanar spacing between the coaxial layers is highest in the case of the lowest diameter MWCNT and slowly decreases with increasing outer diameter. Our HRTEM studies show a decrease in interplanar d002 spacing for MWCNTs having a diameter even much larger than 10 nm. We also looked for a possible variation in the interlayer separation from the inner walls to the outer walls of the MWCNTs. A careful analysis of the HRTEM images reveals that the inner wall separation is about 3% higher than the outer wall separation for a diameter up to 60 nm. However, for very large diameter (80–100 nm) nanotubes the wall separation first decreases as one moves from the innermost wall to the outer walls and then it again increases near the outermost walls that may be due to the structural defects at the outer walls of the MWCNTs as seen from HRTEM images (not shown).

The variation in d002 spacing with increasing diameter is consistent with our XRD results discussed later. However, the d002 spacing calculated from the XRD analysis is marginally higher than that calculated from HRTEM analysis. XRD results show that d002 for large diameter tubes reduces to 3.45 Å, while the HRTEM images show a value of 3.2 Å. One probable reason for such difference is the possible fluctuations in the spacing associated with the jumps in spacing at points where the helix angle changes [21]. Note that the outer walls of the MWCNTs are less strained than the inner walls. Such a difference in strain may not allow graphitic layers to be equally spaced as those of graphite. The observed d-spacings of 3.2 Å is much smaller than that of even turbostratic graphite. Such low d-spacings may occur, if the energy

<table>
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<tr>
<th>Sample name</th>
<th>Diameter range</th>
<th>Centre of the deconvoluted peaks (in cm−1)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Ratio $\Delta I/I_0$</th>
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<tbody>
<tr>
<td>CNT-7</td>
<td>&lt;10 nm</td>
<td>1351.0 1446.0 1550.0 1572.0 –</td>
<td>5.14</td>
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<tr>
<td>CNT-15</td>
<td>10–20 nm</td>
<td>1351.9 1432.0 1556.0 1572.3 1598.0 0.41</td>
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<tr>
<td>CNT-20</td>
<td>10–30 nm</td>
<td>1354.2 1434.0 1554.6 1572.4 1579.0 0.69</td>
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<tr>
<td>CNT-30</td>
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<td>1351.0 1427.0 1557.0 1572.0 0.74</td>
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<td>CNT-50</td>
<td>40–60 nm</td>
<td>1352.0 1430.0 1552.8 1560.7 1598.0 1.17</td>
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<td>CNT-80</td>
<td>60–100 nm</td>
<td>1352.0 1431.0 1553.0 1568.0 1592.0 1.06</td>
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<td>G-band</td>
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<td>G’’-band</td>
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Table 1 Summary of the fitted Lorentian peaks for D- and G-bands of MWCNTs with different diameter ranges.
gained by the local graphitic staking is less than the energy introduced by the defects associated with the stacking. This is consistent with the experimental observation by Liu and Cowley [22]. We believe that the increase in intershell spacing with decreased nanotube diameter results primarily from the high curvature and associated strain in the lower diameter nanotubes. It is likely that high strain in the low diameter tubes causes structural defects in the nanotube walls that may be charged [23] and it causes coulombic repulsion between the tube walls with charges of the same sign. This would result in a higher d-spacing for the low diameter tubes. On the other hand, in a large diameter MWCNT the interaction among the walls increases with the increase in the number of walls and as a result the interwall separation may decrease, as observed experimentally.

3.2. XRD analysis

XRD pattern of different diameter MWCNTs and the spectral profile is shown in Fig. 2. The (002) peak shown in Fig. 2(a) gradually up shifts from 25.7° to 26.2° as the MWCNT diameter increases from 7 nm to 80 nm. Fig. 2(b) shows XRD peaks assigned to (100) and (101) peaks due to in-plane reflections. Note that due to the low intensity of the (100) and (101) peaks, the XRD data for the region 40°–50° were recorded with high integration time. In addition to these regular features of carbon nanotubes, we also observed a low angle peak at ~12.7° (not shown), found in all the samples which gradually shifts to higher value (12.9°) with increasing diameter. A closer look at the (002) peak shows an asymmetry in line shape. The peak profile can be fitted with two Voigt spectral functions, as shown in Fig. 2(c) and the diameter dependent features are extracted for different samples. The asymmetry is assigned to the presence of different crystalline species. Fitted parameters for peak 2 (being the stronger component) show that the Bragg angle (2θ) gradually increases and the FWHM decreases as the diameter of the MWCNTs increases. The corresponding variation in d_{002} spacing is calculated from the Bragg formula and shown in Fig. 2(d), exhibiting a nearly exponential decay with increasing diameter. The empirical equation for the best fit to the data is given by

$$\hat{d}_{002} = 0.345 + 0.37 \exp(-D / 14.4) \quad \text{for } D \geq 0$$  \hspace{1cm} (1)

where D is the outer diameter of the tube and all the constants are in nm. Eq. (1) is obtained by the least-square fit of the function $\hat{d}_{002} = A + Be^{-C/D}$ to our experimental data (where A, B and C are adjustable parameters) as depicted by the dashed curve in Fig. 2(d). The intershell spacing decreases exponentially and becomes 3.45 Å for the large diameter tubes.

Note that we have observed a gradual decrease of d_{002} value for MWCNTs of average diameter up to 80 nm. This is in contrast to the earlier reports from HRTEM [19] and Raman studies [20] where the change in d_{002} value was observed for a diameter up to 10 nm and 20 nm, respectively. For Raman measurement, it was argued that due to limitation in the penetration depth of the laser beam, higher diameter nanotubes did not show variation in d_{002} spacing. Since the X-rays do not suffer from such limitations, probing of large diameter nanotubes with large number of walls has been possible in the present study and indeed shows variation in d_{002} spacing with diameter, as expected. The XRD results are in close agreement with the HRTEM results.
analysis. The variation in the Bragg angle ($\theta$) with diameter is consistent with the theoretical calculation for curved graphite sheets [11]. Theoretical calculations have shown that as the curvature of crystallites with graphene layers increases the Bragg angle increases monotonically from 26.27° to 26.55° and FWHM decreases from 1.35° to 1.02° [11]. Shift in the Bragg angle ($\theta$) is observed experimentally from 26.5° for graphite to 26° for SWCNTs. Lower diameter MWCNTs have higher curvature in the graphene layers, which are probed by X-rays. Our results from XRD analysis shown in Fig. 2(d) are consistent with the theoretical calculations and HRTEM studies shown in Fig. 1(g–l).

Fig. 2(e) shows the variation of FWHM of peak 2 as a function of tube diameter. It is found to follow an inverse relation with the diameter of the nanotubes, which is actually proportional to the number of layers in the nanotubes walls [12]. The line width of the lower angle component of the (002) peak is relatively broad as compared to the graphitic ones. This asymmetry may arise from the different relative orientations of successive layers of MWCNTs forming walls of various chiralities [24]. Using the (002) peak position, the interlayer spacing is often found to be larger than that of highly ordered pyrolytic graphite.

Structural information of materials is contained in the shape of the observed scattering, rather than simply in the position and intensity of peaks [25]. For carbon nanotubes, there are two likely sources of line shape broadening [12]. First is particle size broadening i.e. diameter distribution and second is the strain broadening resulting from a distribution of d-spacings. In the case of domain size broadening the FWHM is given by [12]

$$\gamma_f = 2(\pi \ln 2)^{1/2} / N d_c,$$

where $N$ is the number of layers and $\gamma_f$ is independent of the order of the reflection.

Whereas the width for strain broadening is given by

$$\gamma_a = \frac{\pi l}{d_c} (\Delta d_c),$$

where $l$ is index of reflection and $\Delta d_c$ is the FWHM of the distribution of interlayer spacing. Thus, line width caused by size distribution and strain (induced by wall curvature) are both inversely proportional to the diameter of the nanotubes. In the present study, line shape analysis for peak 2 in different samples shows that FWHM is not directly correlated with the size distribution. Hence, the strain is primarily responsible for the higher FWHM in lower diameter tubes. Contributions of the two factors can be isolated if the higher order spectra are recorded. As the (004) peak was found to be very weak in our samples, isolation of the two contributions for line shape broadening was not feasible. Thus, the observed diameter dependence of FWHM of the (002) peak is primarily attributed to strain broadening related to curvature of nanotubes.

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**Fig. 2.** XRD pattern of different diameter MWCNTs: (a) graphitic (002) peak at ∼25.7°, (b) graphitic (100) and (101) peaks at 42.9° and 44.4° obtained with high integration time, (c) deconvolution of (002) peak using Voigt line shapes, experimental data shown as symbols and fitted peaks as solid lines, (d) variation of $d_{200}$ spacing, calculated from the position of peak 2, as a function of average diameter, (e) variation of FWHM of (002) peak showing inverse diameter dependence; (f) intensity variation of (002) peak, (g) intensity variation of (101) peak and (h) FWHM variation of (100) peak with nanotube diameter.
Information about interlayer stacking correlations can be obtained from (hkI) diffraction peaks having nonzero h or k values. In a recent study, DWCNTs have been taken as a standard model with an aim to extend the theory to MWCNTs. For bundled DWCNTs, it was found that as the number of walls (N) increases FWHM monotonically decreases following 1/N behavior whereas peak position increases up to N ~ 10 and saturates [9]. The decrease of the interlayer spacing with the increase of diameter of the shells [20] and the inner diameter distribution [26] also modifies the shape of the (002) peaks. The intensity and width of the (002) peaks are related to the number of layers, variations of interlayer spacing, lattice distortions [12,27] and nanotube orientation relative to the X-ray incident beam [15]. Due to the complex interplay of a number of factors deciding intensity, no systematic diameter dependent diffraction intensity profile was found for peak 2 (Voigt component at higher angle) of the (002) reflections from our MWCNTs. However, peak 1 of the (002) peak shows nearly exponential increase in intensity with increasing diameter of MWCNTs, as shown by the dashed curve in Fig. 2(f). This is attributed to the large number of layers present in large diameter MWCNTs.

XRD line profile analysis was performed for the (100) and (101) peaks in a similar way. From fitting, we find that the intensity of the (101) peak increases monotonically with increasing diameter of the MWCNTs, as shown in Fig. 2(g). Experimental data points of intensity vs. the diameter of the (101) peak fit well with a single exponential growth profile. Similarly, the line width of the (100) peak systematically decreases with increasing diameter, as shown in Fig. 2(h). In contrast to the inverse diameter dependence of FWHM for the (002) peak, the experimental data points (circles) for the (100) peak follow an exponential decay with increasing diameter, as shown with the dashed line fit. Thus, the line widths of the (002) peak and (100) peak have different origins. We observed an additional XRD peak at ~12.7° for all samples with different diameters and it shows a small up shift as the diameter increases from 7 nm to 15 nm and then it shows a small and gradual increase as the diameter increases further, as shown in Fig. 2(h).

The D-band peak is due to the breathing modes of \(A_{1g}\) symmetry involving phonons near the K zone boundary. This mode is forbidden in a perfect graphitic material and only becomes active in the presence of disorder [31]. Raman frequency of D-band slightly up shifts with increasing diameter from 1351 \(\pm\) 60 cm\(^{-1}\) to 1354 \(\pm\) 1 cm\(^{-1}\). The FWHM of the D-band is relatively large for the low diameter samples (CNT7, CNT-15 and CNT-20) and then it decreases slightly for the higher diameter MWCNTs. Various forms of carbon can be distinguished by the position and the line width of the D-band. Amorphous carbon has a very broad line width (~100 cm\(^{-1}\)). SWCNTs have a D-band position at 1285–1300 cm\(^{-1}\) and a line width of 10–30 cm\(^{-1}\), and crystalline graphite-like forms have a typical position of 1305–1330 cm\(^{-1}\) and a width of about 30–60 cm\(^{-1}\) [32]. MWCNTs have been reported to behave similar to the crystalline graphite-like forms [33]. In our samples, lower diameter MWCNTs show FWHM intermediate between amorphous carbon and crystalline graphite-like forms of the order of ~80–90 cm\(^{-1}\), whereas the higher diameter tubes show FWHM of D-band close to the crystalline graphite-like forms of the order of ~60 cm\(^{-1}\). We also studied the D-band line shape for SWCNTs with a diameter range of 1–2 nm and found that the FWHM was 13 cm\(^{-1}\). Although the relative intensity profiles of D- and G-band of SWCNTs and low diameter MWCNTs look alike, the FWHM of the D-band clearly distinguishes the two. Fig. 3(d) shows the ratio of intensity of G–(S) to D-band. We found that D-band intensity first decreases with a diameter up to 20 nm, because higher diameter rolled graphitic structure will require less bending and correspondingly less disorder. For a diameter above 20 nm, it again increases because higher diameter MWCNTs have less ordered graphitic ordering as compared to low diameter MWCNTs and SWCNTs. Further, from HRTEM imaging we noticed structural defects on the outer walls of the large diameter nanotubes. It may be noted that with the change of diameter, the change in intensity of D-band is quite small compared to the change in G–(S) band intensity.

3.3. Raman spectral features

Due to a large number of walls in the MWCNTs, we do not observe any measurable intensity for the RBM modes from our samples. A typical Raman spectrum in the range of 1200–1800 cm\(^{-1}\) is shown in Fig. 3(a) for CNT-7 (lowest diameter). The inset shows the spectrum for CNT-80 (highest diameter). Raman spectra for all the samples show two major peaks located at ~1350 and ~1570 cm\(^{-1}\), which are attributed to well known D- and G-bands, respectively. Asymmetry in the shape of G-band suggests that multiple peak components are present in the spectrum. These spectra were deconvoluted using Lorentzian line shapes and typical fitting for CNT-7 and CNT-80 are shown with dashed lines. A summary of the fitting parameters for different Raman peaks and their possible identities for different samples are given in Table 1. Here, we focus on the G-band and D-band that are distinct in all the samples and show clear diameter dependence. The lowest diameter sample CNT-7 shows an asymmetric G–(M) band arising from a metallic component at 1550 cm\(^{-1}\) and a relatively strong semiconducting component G–(S) band at 1572 cm\(^{-1}\). For CNT-7, G–(M) component is found to have a Breit–Wigner–Fano resonance line shape having a coupling strength parameter \(1/\gamma = -0.136\), as obtained by fitting. This is due to the interaction of phonons with continuum of states [30]. Higher diameter MWCNTs show 1/q ~ 0 showing Lorentzian oscillators to be sufficient to fit the spectra. It is found that the low diameter CNT-7 has a strong G-band signal as compared to the D-band intensity. However, CNT-15 and higher diameter samples show a much lower intensity of G-band that it is comparable to the intensity of D-band, which is typical of MWCNT samples. The diameter dependence of the Raman shifts of G–(S) and G–(M) bands are shown in Fig. 3(b), while the intensity data for these two bands are shown in Fig. 3(c). The Raman shift for G–(S) band shows a systematic downshift with increasing diameter of the MWCNTs and the G–(M) band frequency first up shifts and then does not change significantly for higher diameter tubes, as shown in Fig. 3(b). On the other hand, the intensity of G–(S) band first goes down drastically as the average diameter increases from 7 nm to 15 nm and then it shows a small and gradual increase as the diameter increases further, as shown in Fig. 3(c).
the Raman frequency and also the phonon confinement effect that is expected to lower the Raman frequency in lower diameter tubes. This change is, however, in contrast to the changes observed for $G^{-\,(S)}$ band shown in Fig. 3(b). Hence, the change in the $G^{-\,(S)}$ frequency cannot be explained by the curvature effect. However, the observed changes in $G^{-\,(M)}$ band frequency follow the behavior expected from the curvature or size effect. Downshift of $G^{-\,(S)}$ band indicates higher elongation strain in graphitic lattice for lower diameter MWCNTs. This is consistent with the lower Raman shift of $G^{-\,(S)}$ observed for lesser compressed SWCNTs studied by applying hydrostatic pressure [34]. In the case of graphene, $G^{-\,(S)}$ band Raman shift has been observed to downshift with increasing number of graphene layers [35]. Lesser elongation strain and higher number of graphitic layers for higher diameter MWCNTs contribute to the downshift of the $G^{-\,(S)}$ band.

It has been suggested that $G$-band frequency is affected by the interlayer spacing, which are correlated to the interlayer spacing. However, no shift in D-band frequency was observed in graphene with increasing number of layers. The authors reported a strong decrease of D-band intensity with increased number of graphene layers. For MWCNTs, we observed a slight decrease in intensity of D-band with the increase in diameter up to 20 nm. In low diameter MWCNTs, large strain in the tube walls may lead to breakdown of translational symmetry in the lattice and a corresponding increase in D-band intensity up to a certain diameter. In large diameter MWCNTs, as the number of layers increases the outer walls are less strained leading to some reduction in the D-band intensity. However, in very large diameter MWCNTs structural defects are present in the outer walls that cause a slight increase in intensity of D-band. To explain the downshift of $G^{-\,(S)}$ band frequency with diameter in MWCNTs, it is clear that as the number of walls increases the interlayer spacing decreases as evidenced from HRTEM as well as XRD analysis. Thus, the observed decrease in G-band frequency with increasing diameter is a result of increased interaction among the closely spaced walls of nanotubes. Computational study on the interwall interaction has been reported for DWNTs and interaction energies were found to be in the range of 13–25 meV/atom [36]. However, no relevant data is available for the MWCNTs. For large diameter MWCNTs, due to closely spaced walls the interaction energy is likely to be significant and Raman analysis allows probing of such interaction only qualitatively.

Further, the effect of diameter on the higher order Raman modes are studied and results are shown in Fig. 4. Raman frequency of 2nd order G-$\prime$ band of low diameter (7 nm) nanotubes is 18 cm$^{-1}$ downshifted as compared to other higher diameter MWCNTs, as shown in Fig. 4. A proper estimation of the peak position was achieved by fitting a single Lorentzian line shape (solid line) to the experimental data (symbols) in each case. The G-$\prime$ mode frequency shows a large up shift as the average diameter increases from 7 nm to 15 nm and then shows slow decrease with diameter for higher diameter nanotubes, as shown in the inset of Fig. 4. Note that the error bar in the data is quite small compared to the magnitude of shifts observed with change in diameter. The lowest diameter MWCNTs show Raman spectral profile close to that of SWCNTs. Intensity of the G-$\prime$ mode first decreases as the diameter increases up to 30 nm and then slowly increases with increasing diameter. Thus the observed spectral features in the Raman data are characteristics of diameter dependence of the MWCNTs. However, observed Raman shifts with diameter are a definite signature of interwall interaction in MWCNTs. Results of our XRD analysis are well corroborated by the HRTEM analysis and fully consistent with the Raman analysis. In contrast to the previous report, we find that Raman
Raman spectral features are not discernable for diameters above 10 nm. On the other hand, the XRD probing does not have any such limitation. Through this study, we have demonstrated the power of XRD and Raman analysis in understanding the contribution of interwall interactions and tube curvatures in MWCNTs as a function of a diameter up to 100 nm. It may be noted that CNT-20 sample having the largest size distribution (10–30 nm) shows some deviations in XRD and Raman profiles as compared to the other samples. Our preliminary studies on thermogravimetric analysis of CNT-20 reveal that various phases of carbon are present as impurities in CNT-20 and due to the presence of other forms of carbon, any deviation from systematic behavior is expected from such samples.

Our Raman results are consistent with a recent report where it was observed that the G band frequency decreases with increasing tube diameter for diameters <20 nm and then saturates [20]. However, we have performed deconvolution of the G-band and analyzed the line shape and diameter dependencies of metallic and semiconducting components separately. Hence, the observed behaviors are, though qualitatively same, but quantitatively different. It was shown that Raman spectral features are not discernable for diameters above 20 nm. However, the present study reveals that features in the G band are sensitive up to an average diameter of 80 nm. Since the penetration depth of the 488 nm laser is of the order of radius of the large diameter MWCNTs used in this work, diameter dependence is easily probed by both the Raman as well as in XRD measurements. Our conclusion is clearly supported by HRTEM analysis.

G band frequency of MWCNTs is affected by the interlayer spacing, as calculated by changes observed in XRD profiles. The d_{200} spacing decreases with the increasing diameter of the MWCNTs even for the largest diameter nanotubes. The shift in the Bragg angle 2θ and the FWHM of the peak show clear diameter dependence. These spectral features can be used to estimate the average diameter for samples with unknown diameter and relative contribution of interwall interactions and tube curvature in large diameter MWCNTs. This is the first report demonstrating that simple XRD measurements can provide valuable information about average diameter and interwall separation in MWCNTs. This technique may not be so useful in the case of SWCNTs since the number of atoms participating in the scattering event is too small as compared to that in MWCNTs and hence poor signal to noise ratio is obtained.

Large intensity of G band in CNT-7 is analogous to the SWNT behavior, where the G-band signal is very high compared to the D-band signal. Thus the low diameter MWCNTs behave like large diameter SWCNTs, while higher diameter MWCNTs behave in a different way due to strong interaction among tube walls. As the number of graphitic layers increases, interaction between different layers becomes significant. This seizes the in-plane motion of cylindrical graphene layers in a MWCNT leading to sudden drop of I_{G}/I_{D} ratio as for CNT-15. As the diameter of MWCNTs increases further lattice strain gets reduced, leading to decrease of number of sp² carbon required for a stable tubular structure [37]. Due to the reduced strain, the intensity of the D-band slightly reduces and correspondingly the I_{G}/I_{D} ratio slowly increases for MWCNTs of diameter >15 nm. Thus, the phonon spectra of the lowest diameter MWCNTs are similar to that of SWCNTs due to participation of a few walls in the lattice vibration.

4. Conclusions

We presented a systematic analysis of the diameter dependent spectral features in XRD and Raman spectra of MWCNTs. XRD results showed exponential decrease in d_{200} interwall spacing with increasing diameter of the MWCNTs, which is fully consistent with the HRTEM observations. Decrease in FWHM of the XRD profile with increasing diameter is consistent with lower strain/curvature of larger diameter nanotubes. Deconvolution of the Raman spectra for different diameter MWCNTs shows gradual decrease of the semiconducting component of the G band frequency with increasing diameter that has been explained on the basis of intertube interactions. Our studies clearly show that phonon spectra of low diameter MWCNTs are similar to that of the SWCNTs and for large diameter nanotubes, intertube interactions become significant. These results demonstrate the capability of XRD and Raman line profile analysis for understanding the intertube interactions for large diameter nanotubes and it further allows probing the strain and curvature effect for the small diameter nanotubes. This study further demonstrates the feasibility of nondestructive evaluation of average diameter and interwall separation in MWCNTs. In the absence of any well defined tool for studying MWCNTs and from the observed diameter dependence of various spectral features, we conclude that XRD is a very powerful tool to characterize MWCNTs.

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