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Raman active modes of single-wall boron nitride nanotubes inside carbon nanotubes

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Abstract: The structure of boron–nitride nanotubes (BNNTs) is very similar to that of CNTs, and they exhibit many similar physical and chemical properties. In particular, a single walled boron nitride nanotube (BNNT) and a single walled carbon nanotube (CNT) have been reported. The spectral moment's method (SMM) was shown to be a powerful tool for determining vibrational spectra (infrared absorption, Raman scattering and inelastic neutron-scattering spectra) of harmonic systems. This method can be applied to very large systems, whatever the type of atomic forces, the spatial dimension, and structure of the material. The calculations of vibrational properties of BNNT@CNT double-walled hybrid nanostructures are performed in the framework of the force constants model, using the spectral moment's method (SMM). A Lennard–Jones potential is used to describe the van der Waals interactions between inner and outer tubes in hybrid systems. The calculation of the BNNT@CNT Raman active modes as a function of the diameter and chirality of the inner and outer tubes allows us to derive the diameter dependence of the wave number of the breathing-like modes, intermediate-like modes and tangential-like modes in a large diameter range. These predictions are useful to interpret the experimental data.

Keywords: RAMAN, CARBON, BORON NITRIDE, SMM, NANOTUBE.

Introduction

Single-wall carbon nanotubes (SCNTs) have gained the attention of many experimental, theoretical, and computational research groups. Such nanomaterials have rapidly evolved into one of the most fundamental structures in nanoscience and nanotechnology since their discovery by Iijima [1]. Single-wall Boron nitride nanotubes (SBNNTs) [2] are intriguing nanotube materials consisting of hexagonal boron nitride sheets. One of the most important features of SBNNTs is that BNNTs possess a large band gap (around 6 eV) irrespective of the diameters and chiralities [3]. In addition, SBNNTs are chemically and mechanically stable [4].

Recently, SBNNTs inside SCNTs (SBNNT@SCNT) are synthetized with a high yield using a nano-templated reaction and ammonia borane complexes as a precursor [5]. In order to study the vibrational properties of SBNNT@SCNT, the Raman active modes are calculated. We present the calculated Raman spectra in the breathing-like Mode (BLM), intermediate-like mode (ILM) and tangential-like mode (TLM) ranges. Also, we report the frequency dependence on the nanotubes diameter. The results are useful in the interpretation of experimental Raman data of SBNNT@SCNT.

Models and methods

The structure of a SBNNT@SCNT consists of SBNNT inside SCNTs greatly spaced by intermolecular distance d close to 0.34 nm from minimum energy calculations. The intratube interactions are described by using a force constants model and previously used in our calculations of the Raman spectrum of isolated SBNNTs [6] and SCNTs [7,8].Van der Waals interaction between the inner SBNNT and outer SCNT is described by the Lennard-Jones potential, given by the following expression:

$$U_{LJ}(r_{ij}) = 4\epsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6})\right] \qquad (1)$$

A Lennard-Jones potential is used to describe the van der Waals intertube interactions between the inner SBNNT and outer SCNT, where rij is the distance between atoms i and j. The parameters of the bond polarizability model are chosen according to Wirtz et al [9]. The energy calculations performed using the Lennard-Jones potential show that the optimal

SBNNT-SCNT distance d is around 0.34 nm. The Raman efficiency of modes is calculated according to the bond-polarizability (BP) model. In this model, the polarizability is only modulated by the nearest-neighbor bonds and the polarizability of a particular bond is assumed to be given by the empirical equation [10]:

$$\chi_{\alpha,\beta}(r) = \frac{1}{3}(\alpha_\ell + 2\alpha_p)\delta_{\alpha,\beta} + (\alpha_\ell - \alpha_p)\left(r_\alpha r_\beta - \frac{1}{3}\delta_{\alpha,\beta}\right) \quad (2)$$

$$\chi_{\alpha,\beta}(r) = \frac{1}{3}(\alpha_\ell + 2\alpha_p)\delta_{\alpha,\beta} + (\alpha_\ell - \alpha_p)\left(\hat{r}_\alpha \hat{r}_\beta - \frac{1}{3}\delta_{\alpha,\beta}\right)$$

Where α and β denote the Cartesian components (x,y,z) and $\hat{r}$ is the unit vector along the vector $\vec{r}$ connecting the atoms n and m which are covalently bonded. The parameters α_l and α_p correspond to the longitudinal and perpendicular bond polarizability, respectively.

The usual method to calculate the Raman spectrum consists of direct diagonalization of the dynamical matrix of the system. However when the system contains a large number of atoms, the dynamical matrix is very large and its diagonalization fails or requires long computing time. By contrast, the SMM allows the Raman spectrum of very large harmonic systems to be directly computed without any diagonalization of the dynamical matrix. This approach is used in previous works [11,12].

Results and discussions

First, we focus on the Raman spectra of BNNT@CNT double-walled hybrid nanostructures. Infinite tubes have been obtained by applying periodic conditions on the unit cells of the two SWNTs. In order to identify all Raman active-modes, we present in figure 1 the calculated ZZ polarized Raman spectra of armchair BNNT@CNT.

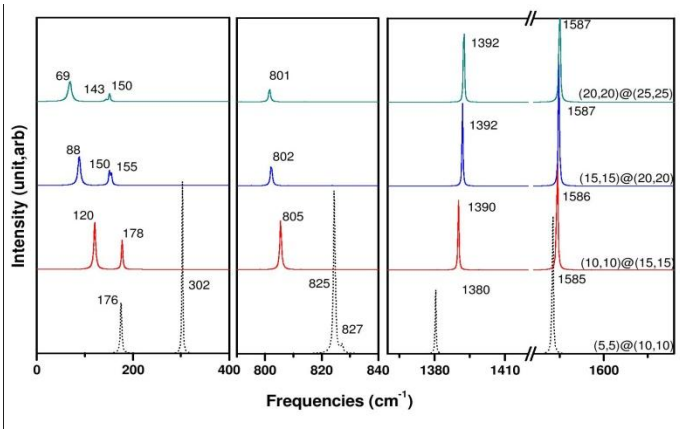

Figure 1: Calculated ZZ polarized Raman spectra of armchair BNNT@CNT: (5,5)@(10,10), (7,7)@(12,12), and (10,10)@(15,15). Spectra are displayed in the BLM (left), intermediate (Middle) and TLM (right) regions.

In all regions of the Raman spectra, our calculations state a systematic frequency upshift of the breathing-like modes in BNNT@SCNTs with respect to SBNNTs and SCNTs due to the van der Waals interactions between the two concentric tubes.

In the TLM region, spectra are characterized by two modes. The number of Raman active modes calculated is independent of the nanotube diameter. We can specify that the modes A1 of BNNT move to the tangential modes CNT, when the diameter increases.

In the intermediate mode region, all spectra are dominated by one mode. We observe a downshift with increasing tube diameter.

In the BLM range, the Raman spectrum shows two modes resulting from the in-phase coupled motions of the breathing modes of the inner and outer tubes. For all modes, we observe a frequency downshift with increasing tube diameter, and the intensity of these modes decreases.

In the case of Zigzag BNNT@CNT (Figure 2), we found that if the diameter of carbon nanotubes increases, the peaks corresponding to BLM mode and those of the intermediate region are downshifted.

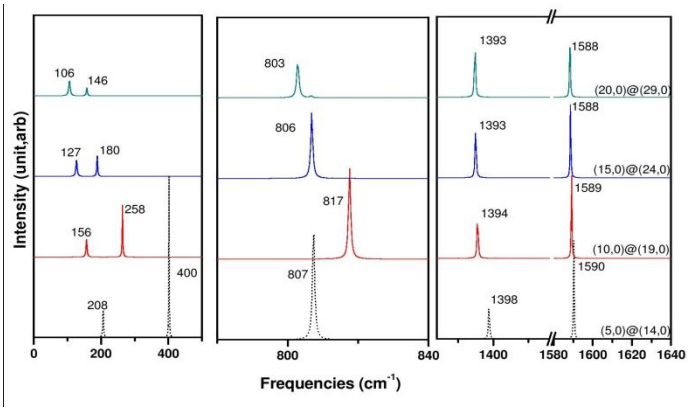

Figure 2: The calculated ZZ polarized Raman spectra of zigzag BNNT@CNT: (9,0)@(18,0), (17,0)@(26,0), and (26,0)@(35,0) in the BLM (left), intermediate (Middle) and TLM (right) regions.

In the intermediate and TLM regions, the same number of Raman active modes in armchair and zigzag SBNNT@SCNT is found.

In the BLM region, a significant dependence of Raman active modes as a function of the tube diameter is calculated. Our calculations state a systematic up shift of the breathing-like mode frequencies with respect to the frequency of the breathing modes in isolated carbon and boron nitride nanotubes. For the A_1 tangential mode of SWBNNT@SWCNT, all the modes downshift with increasing tube diameter (Figure3).

The diameter dependence of the specific RBLMs and especially on the in-phase and counter-phase coupled motions of the RBMs of the inner and outer tubes. These modes are called RBLM(CNT) (in-phase motions of both tubes) and RBLM(BNNT) (counter-phase vibrations of both tubes). For instance, they are, respectively, centered at 165 and 286 cm^{-1} in BNNT(9,0)@(18,0)CNT. Their eigen displacement vectors obtained from the direct diagonalization of the dynamical matrix are displayed in Figure 4.

One can see that the RBLMs modes are strongly dependent on the diameter D, is well fitted by the analytical expression:

$$\omega(\mathrm{cm}^{-1}) = \frac{A}{D} \quad (3)$$

The A parameter depending on the mode symmetry (see table 1) The value of this A parameter is close to 231 and 158 nm cm^{-1} for the RBLM(CNT) mode and RBLM(BNNT) mode respectively (see table 1), independently of chirality.

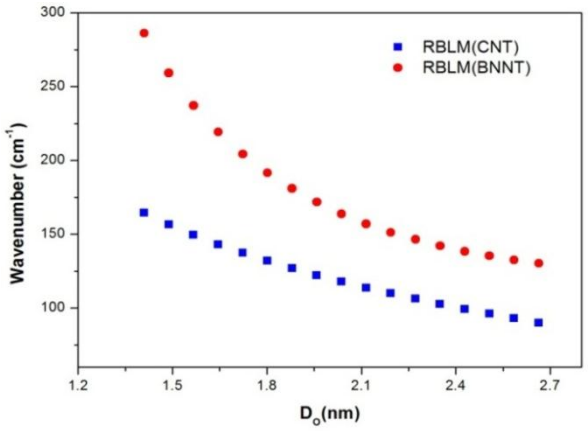

Figure 3: Diameter dependence on the wavenumber ZZ infrared active modes for SWBNNT@SWCNT in the low wavenumber region.

Systems	CNT		BNNT	
Modes	RBLM	RBM	RBLM	RBM
A(nm.cm-1)	231	224[13]	158	190[14]

Table 1 : The A parameter for the A/D dependence of the modes as a function of the tube diameter D.

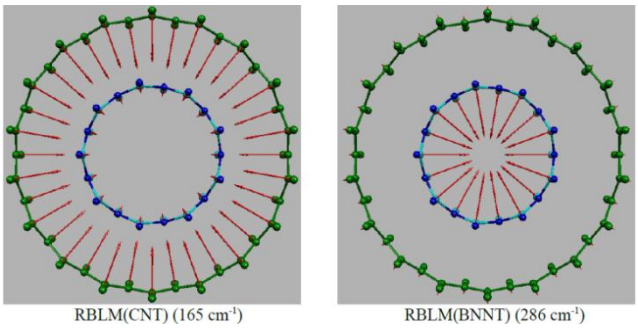

Figure 4: Calculated atomic motions of selected modes in BNNT (9,0)@(18,0)CNT.

Conclusion

In this work, we have calculated the Raman spectra of SBNNT encapsulated inside SCNT using the spectral moment's method. The dependence of the positions of the Raman-active modes in the low, intermediate, and high wave-number ranges as a function of the encapsulated tube diameter are discussed. We found in the BLM range that the Raman spectrum shows two modes resulting from the in-phase coupled motions of the breathing modes of the inner and outer tubes. We observed a frequency downshift with increasing tube diameter, and the intensity of these modes decreases. We found also in the TLM regions, the same number of Raman active modes in armchair and zigzag SBNNT@SCNT. These results are useful in the interpretation of experimental Raman data of SBNNT@SCNT.

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