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Dual distributions for the metallic and semiconducting single-walled carbon nanotubes observed by Raman spectroscopy.

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The prospective applicability of single-walled carbon nanotubes (SWNT) is highly dependent on its controlled synthesis. Effects of few macroscopic growth-conditions (such as catalyst composition, temperature of deposition etc.) reflected on the distributions of SWNT (diameter, chiralities and semiconducting-metallic nature), are studied by Raman spectroscopic analysis. We report the presence of two different diameter distributions for as-grown metallic and semiconducting SWNT, the metallic tubes having larger average diameters than their semiconducting counterpart. We hope that, in future, it should be possible to selectively synthesize SWNT with pre-determined chirality, diameter and metallic/semiconducting nature.

Single-walled carbon nanotubes (SWNT) have unique electrical and mechanical properties to emerge as one of the most promising materials for the future nanoelectronics devices [1, 2]. Depending on the axis of "graphene sheet folding", generally represented by the two chiral integers n and m, SWNT could either be metallic (if $n - m$ is divisible by 3) or semiconducting. This property is of paramount importance in realizing nano-device applications. Although, the separation of metallic and semiconducting species from the bulk mixture of SWNT were successfully carried out by various techniques [3, and references therein], search for preferential synthesis methods are still in progress. Understanding of the physical phenomena during a typical synthesis of SWNT could provide useful information to approach better controllability. On the other hand, the study of as-grown SWNT-samples and their responses to various growth-conditional changes could help correctly model an SWNT-synthesis method. In the present letter we report experimentally observed dual distribution feature for metallic and semiconducting SWNT in the as-grown samples. This separation of distributions, depending on electronic structure, could be correlated with the similar feature of strain energy per atoms of narrow SWNT [4].

For this experimental study, SWNT were grown by catalytic thermal chemical vapor deposition (CVD), using ethanol as the carbon source. The metal catalyst embedded in commercially available Y-type zeolite (HSZ 390 HUA, Tosoh Cor.) was prepared according to the methods of

Mukhopadhyay et al [5]. We have used three catalysts in which the amounts of both the metals, viz. Fe and Co, were 10 wt %, 6 wt % and 2.5 wt % with respect to the zeolite powder. The carbon samples containing SWCN were analyzed using low frequency Raman spectroscopy [NRS-1000HS, JASCO Corp] that is more popularly known as radial breathing mode or simply RBM.

Radial breathing mode of Raman scattering provides valuable information about diameters distribution of SWNT. Through this measurement it is possible to trace out both the metallic and semiconducting type SWNT. Providentially, clear separation exists for the metallic and semiconducting SWNT in the RBM spectrum with a typical excitation frequency. Although, there are tubes with the same diameters (but of different chiralities) corresponding to the same RBM frequencies, in general they respond to different laser excitation frequencies. This makes it easier to assign the chiralities of SWNT-peaks in the RBM Raman spectra. With the standard laser excitations one might find out the possible SWNT that will resonate. Even though the strong bundling of SWNT can shift the Raman peak positions [6], it is possible to assign the chiralities for each SWNT following a proper mapping of chiralities versus excitation energies [7].

The Raman spectrum for each sample was obtained as the average of seven spectra recorded at different locations of the SWNT-sample on view. These spectra obtained in arbitrary units need to be calibrated before its comparison

with another spectra for different samples. In Figure (1) the RBM spectra, obtained by 1.96 eV laser excitation and calibrated by respective G-peak intensities, for three samples grown on 10 wt %, 6 wt % and 2.5 wt % catalyst with respect to zeolite, are compared. No continuous diameter dependent variation in the RBM spectra with changing zeolite to catalyst ratio was observed, unlike reported by Inoue and Kikuchi [8].
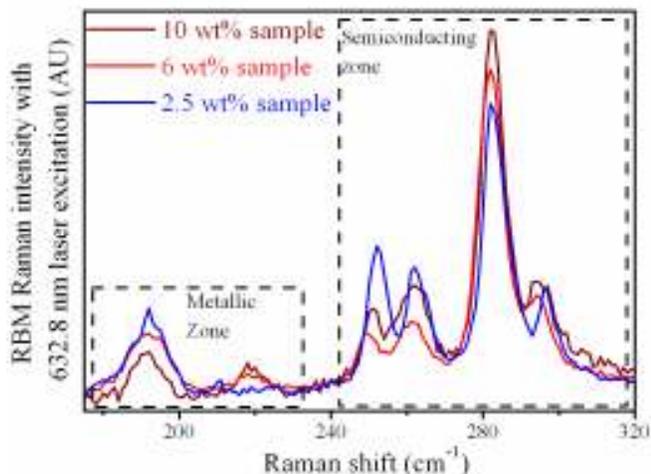

Figure (1) : RBM-Raman spectra (excitation energy 1.96 eV), normalized by individual G-peaks, for three SWNT-samples grown on catalysts with three different metal-catalysts to zeolite ratios at 700 ^{o}C. Boxes indicate metallic and semiconducting zones.

More interestingly, both of the semiconducting and metallic SWNT-distributions shift towards larger diameter region in response to the reduction of metal-catalyst fraction with respect to the zeolite support. Calibrating with respect to the highest intensity for both metallic and semiconducting zones provide the enhanced view of the aforementioned feature (Figure 2). The variation of growth temperature can also modify the diameter distribution of synthesized SWNT [9, 10]. The highest-intensity-calibrated-RBM spectra of three samples grown on 6 wt % catalyst at different temperatures (i.e. 700, 750 and 800 ^{o}C) are shown for metallic (Figure 3*a*) and semiconducting (Figure 3*b*) zones. With the increase in the growth temperature the distribution of semiconducting SWNT were found to shift towards higher diameter regions, as previously reported by Miyauchi et al. via photoluminescence measurements [9]. However, in response to the variation of growth temperature, the group of metallic-SWNT responds oppositely with respect to their semiconducting counterparts. The analysis of RBM Raman spectra reveals discontinuous and sometimes dissimilar responses towards any variation of growth conditions on the basis of electronic structure of the SWNT, i.e. their metallic or semiconducting character. These results indicate the possible existence of dual distributions for metallic and semiconducting type of carbon nanotubes in the as-grown SWNT-samples.

Other than 1.96 eV, the RBM Raman spectrum of SWNT grown on 6 wt % catalyst and at 700 ^{o}C was also monitored using 1.58 eV and 2.33 eV excitations [11]. By multi-peak Lorentz fitting it is possible to assign the chirality for individual peaks. With 1.96 eV laser excitation,

the thickest of the metallic tubes found was ($n = 16$, $m = 1$), whose diameter (d) is estimated to be 1.312 nm (using the relation: $d = 0.249 (n^2 + m^2 + nm)^{1/2}$ nm [12]). While the largest of the semiconducting tubes in the sample was (9, 7), having an estimated diameter of 1.103 nm, obtained by 1.58 eV excitation. Almost no noticeable peaks were found for (9, 8) [$E_{22} = 1.539$ eV, $d = 1.17$ nm], (13, 3) [$E_{22} = 1.62$ eV, $d = 1.17$ nm] and (12, 5) [$E_{22} = 1.57$ eV, $d = 1.201$ nm] in spite of the fact that their optical transition energies are very close to the excitation energy (i.e. 1.58 eV). It could be noted that the RBM-peaks for (11, 0) [$E_{22} = 1.68$ eV] and (10, 2) [$E_{22} = 1.69$ eV] nanotubes by the same excitation energy were obtained with considerable intensities.
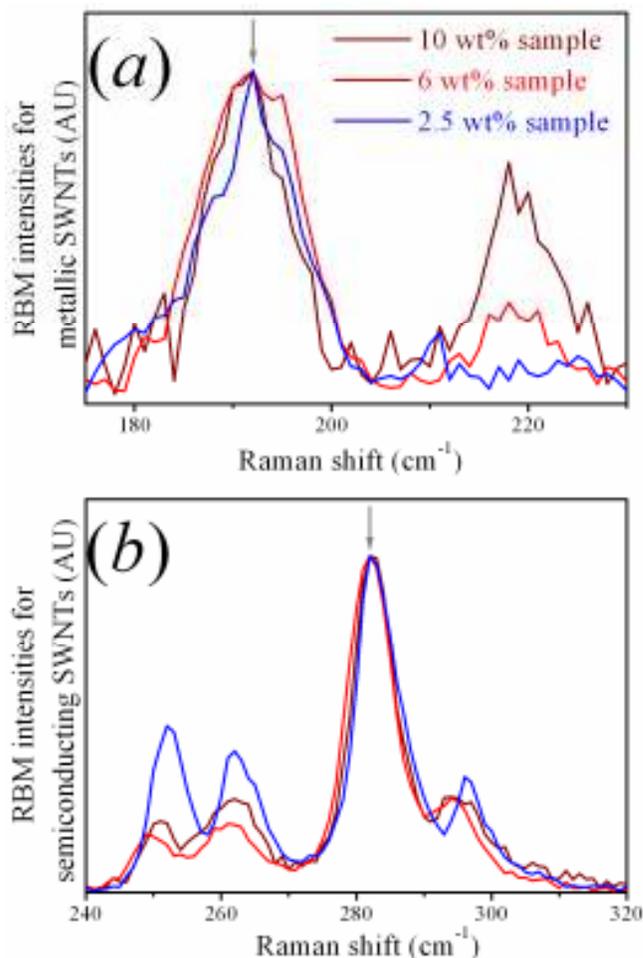

Figure (2) : RBM spectra of (*a*) metallic and (*b*) semiconducting zones for the same samples as of fig.1 are plotted separately, which are normalized with respect to respective highest peaks (indicated by pointers).

However, in case of lower diameter limit for both metallic and semiconducting SWNT of the sample, no perceptible difference in diameter was obtained with the set of excitation energies employed. With these available laser excitations minimum diameter metallic tube found was 0.836 nm [(10, 1)], since it was not possible to probe any further down with 2.33 eV as the highest laser excitation. Minimum diameter traceable for the semiconducting SWNT was 0.757 nm [of chirality (6, 5)].

Nonetheless, the difference in the diameter ranges, particularly at the higher side, for metallic and

semiconducting SWNT in an as-grown sample is again validating the existence of dual distributions. The metallic SWNT-distribution appears to be at the higher diameter region with respect to the distribution of semiconducting SWNT.
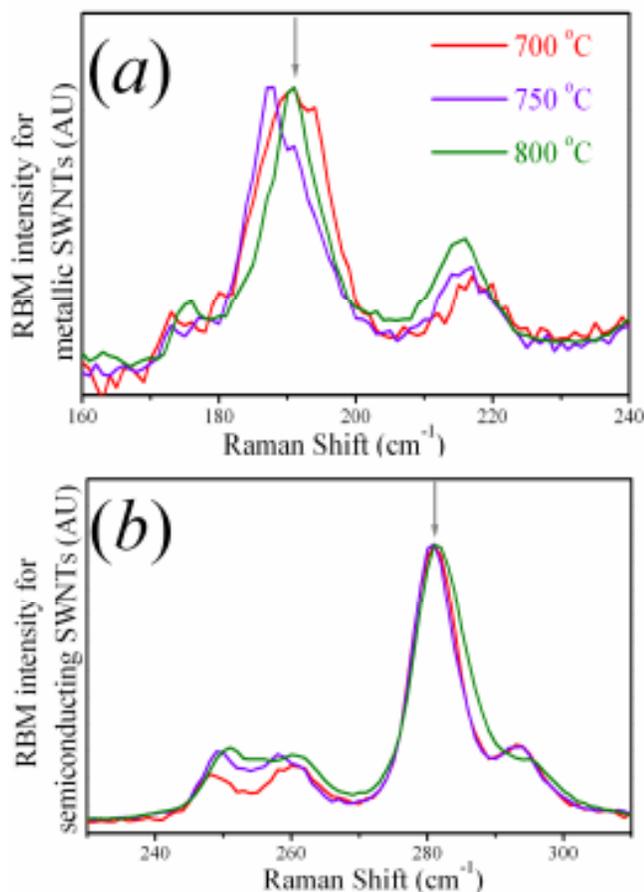

Figure (3) : (*a*) Metallic and (*b*) semiconducting zones of the RBM-Raman spectra, normalized with respect to respective highest peaks (indicated by pointers), for three SWNT-samples grown at three different temperatures.

The strain energy per atom of low-diameter SWNT deviate from their values calculated using continuum elastic theory that assumes rigid non-modifying hexagonal graphene unit while folding. Consequently, as the curvature increases, the strain energy per atoms of SWNT gradually starts depending on their chirality and the electronic structures; metallic tubes having the larger energy per atom compared to their semiconducting companions [4]. The amount of energy per atom is of the same order of thermal energy, when energy is entirely supplied thermally as in the case of thermal CVD-synthesis of SWNT. It will be logical to consider that for the formation of SWNT, this amount of energy per atom should be supplied. And accordingly the SWNT, which have the strain energy per atom close to the applied thermal energy, are more probable to grow. From this presumption it is expected that for a particular growth temperature, mean diameter of the metallic-SWNT distribution will be larger than that of semiconducting SWNT, which could explain our experimental observation. Apparently, the probabilistic distribution of SWNT determined by the temperature and other conditions, such as

the choice of metal catalysts/support material and their size distribution, the source gas and its supply rate etc. could play crucial roles in further modifying the SWNT-distribution in terms of its width and the mean diameter. This qualitative SWNT-synthesis hypothesis gets justification from the fact that the ultra-thin SWNT, having larger strain energy per atom, requires large thermal energy for synthesis [13-15]. However, with slight increment in thermal energy in the comparatively higher diameter range, the SWNT-distributions have found to shift towards larger diameter [Ref. 9, 10 and semiconducting SWNT-distribution in this work]. This discrepancy could not be explained from the proposed qualitative arguments. It might be associated with the chiral dependence of the strain energy per atom.

The experimental evidence of the existence of separate distributions for metallic and semiconducting SWNT, in the synthesized samples, could lead to newer ways of controlled synthesis on the basis of electronic-structures. Apparently, the potential energy selective growth principle seems to be one of the candidates for such a feature. According to this representation, with the reduction of the mean diameter, the SWNT-distribution gradually becomes narrower. However, for getting a comprehensive picture of any growth mechanism, the effects of these growth conditional changes on the chirality distributions of as-grown SWNT-samples need to be monitored carefully.

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Supplimentary Information :
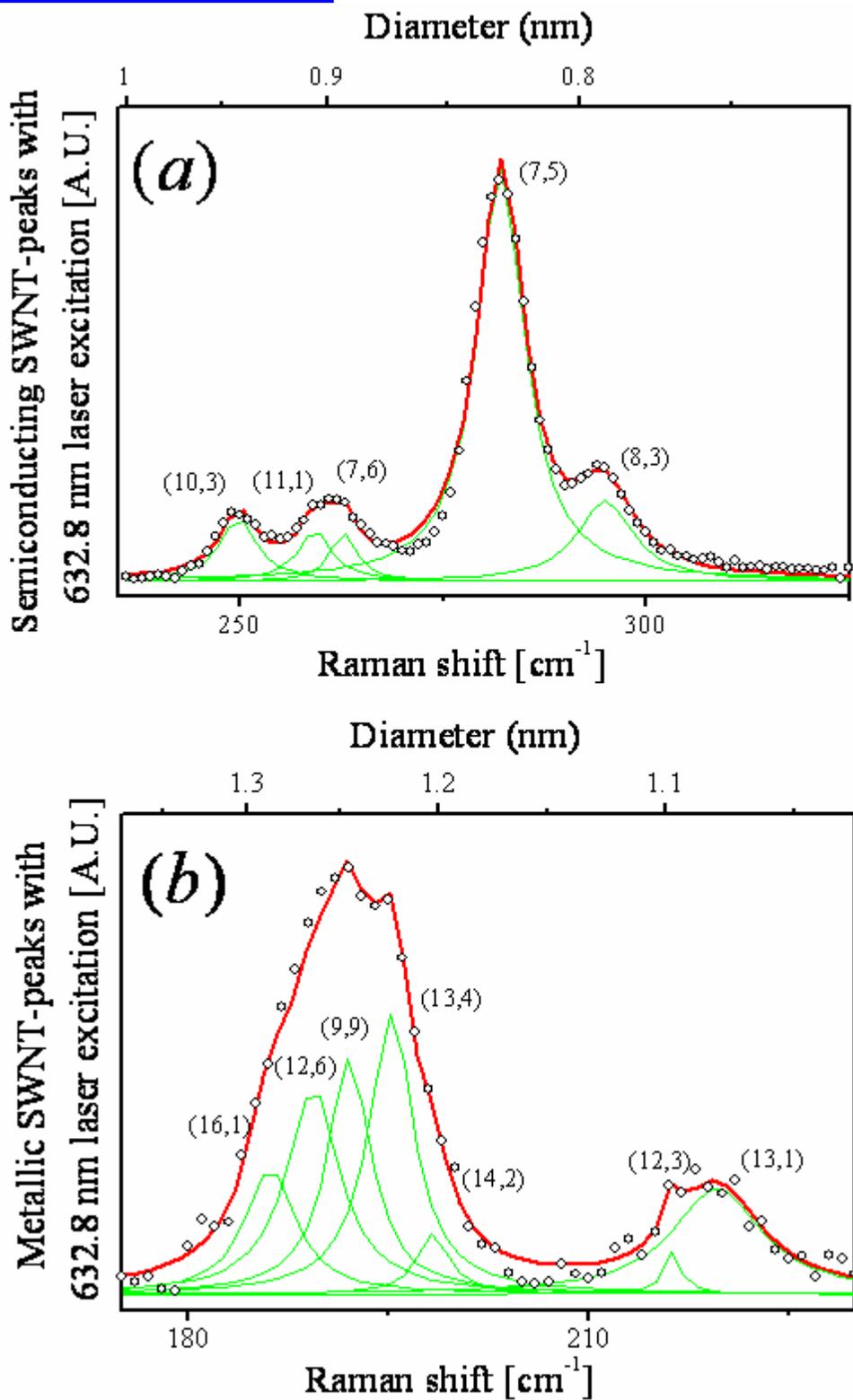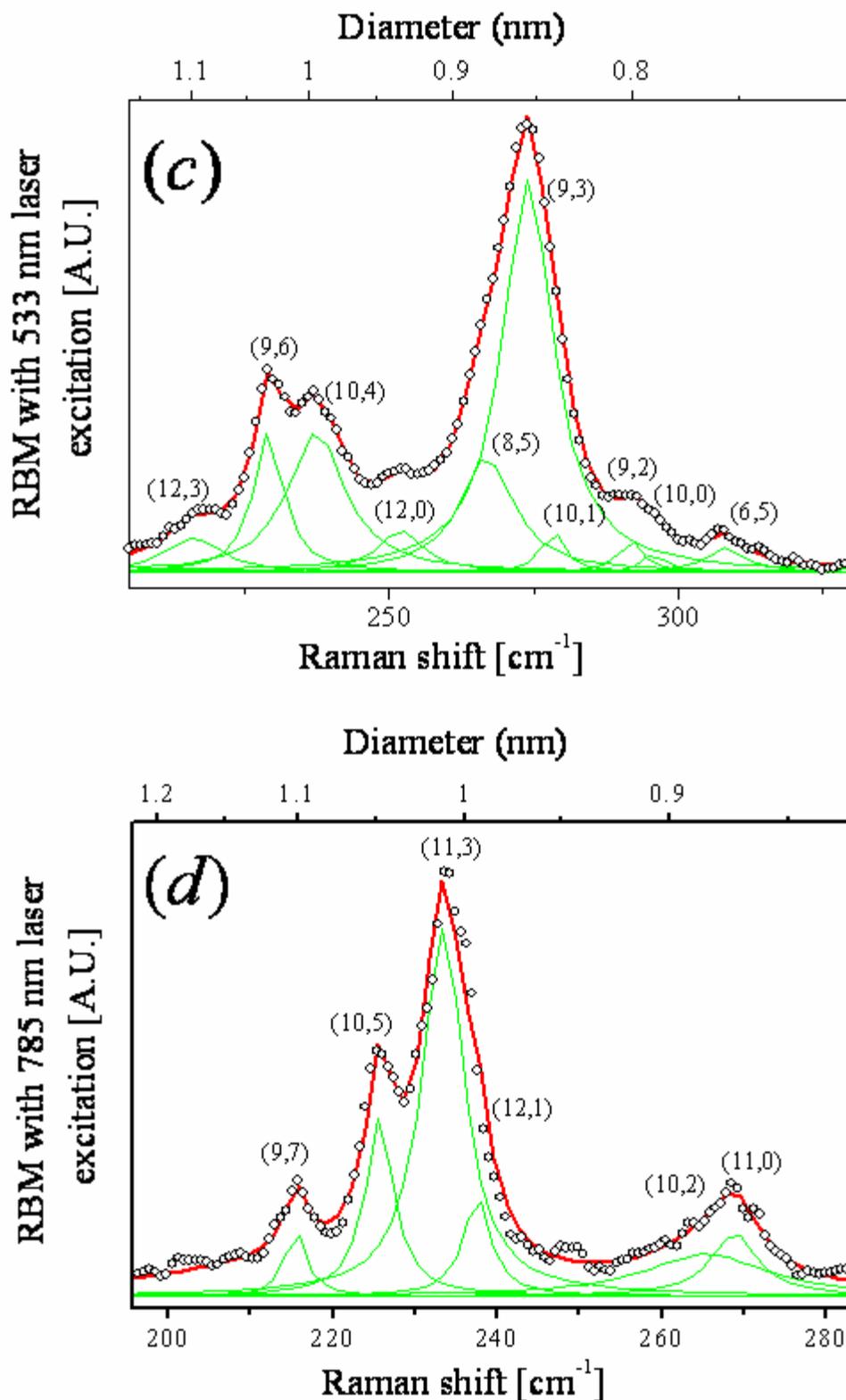
Radial breathing mode spectra of SWNT, for the sample grown on 6 wt. % catalyst at 700°C, using three different laser excitations (written in the respective axis titles) are plotted with respect to Raman shift (bottom scale) and diameter (top scale). Lorentzian fitting for individual nanotubes (chiralities are indicated in brackets) are shown along with the net profile (red line). Experimental data are shown as scattered circles.