Raman scattering on DWCNT filled with 1D CdSe nanowire

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Unpolarized Raman spectra of radial and tangential modes on DWNTs filled with 1D nanocrystalline CdSe semiconductor excited with 514.5 nm were studied at room temperature. In the low wavenumber region, we observed several phonons which correspond to the inner and outer radial modes of DWNTs, the confined LO and TO CdSe phonons and surface optical modes of CdSe nanowires.

Keywords: Carbon nanotubes; nanowires; confinement.

Se estudio el espectro Raman no polarizado a temperatura ambiente de los modos radiales y tangenciales de nanotubos de carbono de doble pared rellenos del semiconductor CdSe nanocristalino 1D, excitado con 514.5 nm. En la región de bajo número de onda observamos varios fonones que corresponden a los modos radiales de los tubos internos y externos, los fonones ópticos confinados LO y TO y fonones ópticos superficiales del nanoalambre de CdSe.

Descriptores: Nanotubos de carbon; nanoalambres; confinamiento.

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1. Introduction

Carbon nanotubes have attracted intense scientific interest due to their fascinating essentially one-dimensional electronic and vibrational band structure, their unique mechanical properties as well as the prospect for numerous applications. Raman spectroscopy has become a widespread tool for the analysis and characterization of carbon nanotubes, and numerous Raman scattering studies on single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes have made important contributions towards the understanding of the physical properties of these materials [1–3]. Raman spectroscopy at ambient pressure has also been successfully employed in the study of the more recently observed [4] and synthesized in bulk quantities [5] double-wall carbon nanotubes (DWNTs), suggesting that the outer tubes provide an unperturbed environment to their interior [6] and that the interaction in a DWNT bundle is stronger than the inner-outer tube interaction [7, 8]. Semiconductors can be introduced into carbon nanotubes (CNTs) by capillarity. These experiments have made possible the study of low-dimensional crystal growth when the incorporated material is constrained to a few atomic layers in thickness by the encapsulating van der Waals surface of the carbon nanotubes. The preparation of highly anisotropic one-dimensional (1D) structures confined into CNTs in general is a key objective in carbon nanotube research [4,5]. In this work, we study DWNTs filled with CdSe by Raman spectroscopy in order to investigate their structural stability and the confinement effect in the inner nanowire.

2. Experiment

Raman spectra of the DWNTs were recorded in the back-scattering geometry using a micro-Raman, triple grating system (DILOR XY800) equipped with a cryogenic CCD detector. The spectral resolution of the system was about 1 cm$^{-1}$. For excitation, the 514.5 nm line of an Ne laser was focused on the sample by means of a 100x objective, while the laser power was kept below 2 mW in order to eliminate laser-heating effects on the probed material and the concomitant softening of the observed Raman peaks [9, 10]. The Raman spectra of radial, tangential and second order modes was measured in empty and filled DWCNT. The phonon frequencies were obtained by fitting Lorentzian functions to the experimental peaks.

3. Results and discussion

Double-wall carbon nanotubes were prepared by the technique developed by Flahaut and co-workers [5]. A systematic analysis of TEM images reveals that samples produced by this method contain approximately 77% of DWNTs; the high proportion of DWNTs was also confirmed by electron diffraction [9] with a small admixture of about 18% single-wall carbon nanotubes (SWNTs) and roughly 5% triple-wall carbon nanotubes [5]. We also observed that the nanotube was partial CdSe filled (about 60%) and the length of encapsulated grains are always bigger than the diameter of the inner CNT. The DWNTs filling is made by "capillary technique". It consists in introducing in a quartz glass the product of interest and DWNTs. The temperature is raised up to a few degrees above the fusion point of CdSe, and the sample is then cooled down slowly ($< 1^\circ$C per minute). In this way, we obtain a confinement of CdSe inside the DWNT. The excess CdSe surrounding the CNTs was removed by sonicating the filled nanotubes in a concentrated NaOH solution (6N) for a short
time, immediately followed by filtration on a polycarbonate membrane \cite{5}. At normal pressure, from the analysis of Raman spectra \cite{5}, the tangential mode frequency of the external semiconducting tubes represents the unresolved $A_1$ and $E_1$ tangential modes, and the internal semiconducting tubes in DWCNTs is associated to the $A_1$ tangential mode and can be separated, respectively, into 1595 cm$^{-1}$ and 1568 cm$^{-1}$, (see Fig. 1). The observed difference between the spectrum of the empty and filled nanotubes is in the range of the spectral resolution of the system, which indicates that the nanowire does not affect the tangential movement of the carbon atoms in the surface of the nanotube. From the analysis of the spectral lines, we concluded that in these DWCNTs there is a high proportion of semiconductors. The intensity ratio between the defect D band (1347 cm$^{-1}$) and the G bands allows us to conclude that the defect concentration in these nanotubes is very low.

In the low wavenumber region, we observed several phonons which correspond to the inner and outer radial modes of DWNTs, the confined LO and TO CdSe phonons and surface optical modes of CdSe nanowires, [see Fig. 2].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Raman spectra of tangential region for CNT filled and empty.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Raman spectra of low wavenumber region for CNT filled and empty.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Confinement effect on the LO phonon CdSe.}
\end{figure}

The phonon confinement should affect the phonon energy (red shift) and asymmetry on the low frequency side. These results are in accordance with the dispersion curves of bulk CdSe: negative dispersion of the LO phonon and very small positive dispersion of the TO phonon \cite{14}.

Following the scheme suggested in \cite{11}, from the analysis of radial phonons, we obtained the diameter of the inner and outer carbon nanotubes (0.91 < $d_{\text{inner}}$ < 1.37 nm, 1.59 < $d_{\text{outer}}$ < 2.05 nm) and also the chiralities. These assignments are observed in Table I.

To study the confinement effect in the LO phonon CdSe, we can use the confinement model proposed by Richter et al. \cite{12} and Campbell Fauchet \cite{13} to study the diameter ($d$) of the nanowire. In this model, the first order Raman spectrum is given by

\begin{equation}
I(\omega, d) = A \int_0^{2\pi/a} \frac{q^2 |C(q)|^2 dq}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2},
\end{equation}

where $A$ is the intensity prefactor, $\omega(q)$ is the phonon dispersion curve, $\Gamma_0$ is the natural full width at half maximum (FWHM), including the instrumental resolution, and $C(q)$ is the Fourier component of the phonon confinement function, which is taken as Gaussian, this is,

\begin{equation}
|C(q)|^2 = e^{(-q^2\pi)^2}
\end{equation}
TABLE II. Length of CdSe nanowires

<table>
<thead>
<tr>
<th>( \omega_{SO} )</th>
<th>( l )</th>
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<tbody>
<tr>
<td>173.51</td>
<td>5.95 nm</td>
</tr>
<tr>
<td>180.31</td>
<td>2.61 nm</td>
</tr>
<tr>
<td>187.77</td>
<td>0.95 nm</td>
</tr>
</tbody>
</table>

Fitting Eq. 1 to the experimental confined LO raman peak (see Fig. 3) and using the CdSe phonon dispersion curves which have been reported in Ref. 14, we obtain a nanowire diameter of the order of \( d \approx 0.88 \) nm. This value is smaller than the diameter of the inner nanotube, which suggests that the nanowire is inside of DWCNT.

The SO phonons in nanowires CdSe can be studied with the dispersion relation \( \omega_{SO}(q) \) for a SO mode in an infinite long cylindrical wire [15], in the limit where the phonon wavevector \( q \gg \omega/c \), given by

\[
\omega_{SO}^2 = \omega_{TO}^2 - \frac{\epsilon_\infty (\omega_{LO}^2 - \omega_{TO}^2)}{\epsilon_\infty + \epsilon_m f(x)}; \quad x = qr
\]  

(3)

where \( \omega_{TO} \) and \( \omega_{LO} \) are the TO and LO modes frequency at zone center, \( \epsilon_\infty \) is the high-frequency dielectric constant of bulk CdSe, \( r \) is the wire radius, and \( f(x) \) is obtained from the eigenvalue equation

\[
f(x) = \frac{I_0(x) K_1(x)}{I_1(x) K_0(x)}
\]  

(4)

Here \( I_j(x) \) and \( K_j(x) \) are Bessel functions. We can use Eq. (3) to obtain the value of \( q \) for the different SO phonons and to determine the length scale which is responsible for excitation of the SO mode given by \( 2\pi/q \). Table II presents the values obtained. The different lengths observed in the CdSe nanowires corresponds to the lengths of the encapsulated grains inside the CNT.

4. Conclusions

In conclusion, we have carried out a detailed Raman measurements of DWCNTs filled with nanowires of CdSe, and the diameter obtained for the CdSe nanowires indicated that it is contained inside the inner carbon nanotube. Based on a theoretical model for SO phonons in a cylindrical wire, we have estimated the length of CdSe nanowires encapsulated inside the CNT. These results are in agreement with the TEM measurements.

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