Combined Raman Spectroscopy and Transmission Electron Microscopy Studies of a NanoBud Structure

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Fullerenes[1] and carbon nanotubes (CNTs)[2] have attracted a great interest in the research community due to their remarkable properties and potential applications. Recently, we have discovered a novel hybrid material that combines fullerenes and single-walled carbon nanotubes (SWCNTs) into a single structure in which the fullerenes are covalently bonded to the outer surface of the SWCNTs, called NanoBuds.[3] This new material showed a high cold electron field emission efficiency, thus making it attractive for many electronic applications, such as flat panel displays. In the previous reports,[3,4] we have confirmed the NanoBud structure by transmission electron microscopy (TEM), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF), UV−vis absorption spectra, scanning tunneling microscopy (STM) and spectroscopy (STS) measurements. However, due to the low symmetry and wide distribution of fullerenes in the NanoBud samples, until now, no feature from fullerenes has been detected with Raman spectroscopy.

In this communication, we present a combined Raman and TEM study of an individual freestanding NanoBud structure. Focusing on the single NanoBud structure instead of a bulk powder sample allowed us to observe for the first time the characteristic features of both SWCNT and fullerenes in the Raman spectrum. Moreover, the atomic structure of the CNT was determined independently by electron diffraction (ED) and Raman spectrocopy.

The NanoBud samples were synthesized in a one-step continuous process based on ferrocene vapor decomposition in a CO atmosphere.[4] The key parameter required for the NanoBud synthesis was found to be the presence of trace concentrations of H_2O vapor or CO_2 as etching agents. For the formation of the NanoBud structure, initially, a certain number of pentagons should be generated for fullerene formation. The formation route of those pentagons, promoted by the presence of etching agents, is expected to determine the formation of fullerenes on the surface of CNTs.[4] The NanoBud sample used in this study was produced at 900 °C with 2000 ppm introduced CO_2. The product was collected downstream of the reactor on a TEM grid using an electrostatic precipitator.[5] The as-obtained product on the TEM grid was directly investigated with the Raman spectrometer (Wintech alpha300) and TEM (Philips CM200 FEG), respectively. The holes of the lacey carbon film on the TEM grid are visible in the optical microscope, so the comparison with the overview TEM images can recognize the same hole and further the area where the tube sits. The room-temperature Raman spectra were performed using a frequency doubled Nd:YAG green laser ($\lambda = 532.25$ nm) and Olympus 100 × air objective. Once the CNT is in resonance with the laser energy, the full Raman spectra are recorded. The laser power impinging on the NanoBuds was measured to be 68 μw, and the laser spot size was about 200 nm. The electron diffraction experiment was carried out with the TEM operating at 80 kV with a Gatan 794 multiscan CCD camera (1k × 1k).
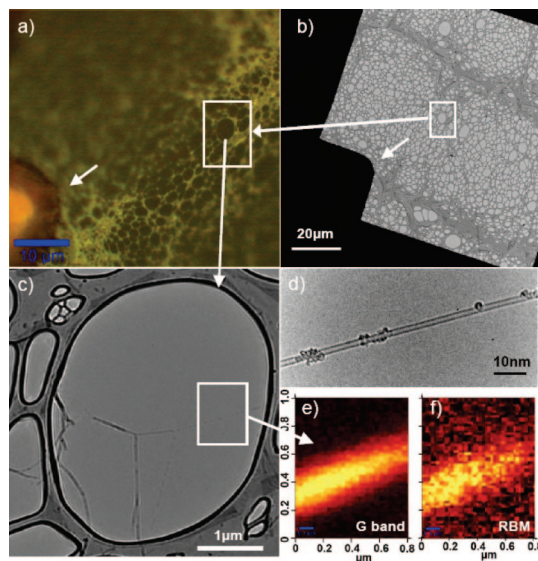

Figure 1. (a) Optical microscope and (b) low-magnification TEM images of the same hole in a TEM grid square. (c) An intermediate magnification TEM image of the hole bridged by NanoBuds. (d) A high-resolution TEM image of an individual SWCNT covered by fullerenes. Raman map of (e) G band (1562−1613 cm^{-1}) and (f) RBM (125−143 cm^{-1}) region on the area of 1 × 0.8 μm (framed in (c)).

From the optical microscope image (Figure 1a) and the low-magnification TEM micrograph (Figure 1b), the outshoot (pointed by small arrows) in the left bottom corner of the TEM grid square was used to locate the hole where the investigated tube was bridging. Carefully comparing with the intermediate magnification TEM images, it is feasible to corroborate that the Raman investigations were carried out on the same hole. The high-resolution TEM image (Figure 1d) reveals clearly a NanoBud structure, that is, fullerenes attached to the surface of an individual SWCNT. In order to find the precise position of the NanoBuds, we performed Raman mapping on an area of 1 × 0.8 μm (framed in Figure 1c) on the determined hole. Raman maps were acquired integrating the Raman signal in the 1562−1613 and 125−143 cm^{-1} spectral region, which correspond to G band (Figure 1e) and radial breathing mode (RBM) (Figure 1f), respectively. It is easy to locate the NanoBuds in submicron scale in Raman maps. Localizing the laser spot right on this individual NanoBud structure, we recorded the Raman spectrum shown in Figure 2.

Regarding the freestanding individual SWCNT, the high I_G/I_D ratio (∼30) indicates the low defectiveness in the SWCNT. It is worth mentioning that the presence of this D band also suggests the NanoBud structure. Given the fact that even a low amount of exohedral bonded carbon leads to an increase of the intensity of
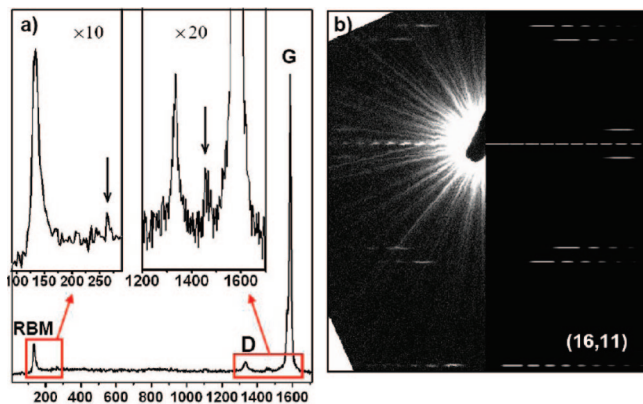
Figure 2. (a) Raman spectrum of the NanoBud structure (shown in Figure 1d) obtained at ambient conditions using green laser excitation (2.33 eV). The spectrum revealed the presence of RBM at 133 cm^{-1}, D and G modes, and the arrows indicate the fullerene features at 264 and 1465 cm^{-1}. (b) Electron diffraction pattern of the same nanotube assigned as (16,11) (left: experimental, right: simulated image).

the D band, the covalent bonding that attaches fullerenes to the surface of the SWCNT cannot be ruled out in this contribution. A single narrow RBM is observed at 133 cm^{-1}, based on the equation $\omega = 223/d + 10$,[6] the calculated diameter of the SWCNT is 1.81 nm. The detectable signal for 2.33 eV incident energy means that the transition energy of the SWCNT is close to 2.33 eV. Following the references,[7,8] one can assign this SWCNT as the (16,11) semiconducting nanotube.

On the same freestanding tube, we conducted electron diffraction experiments. A half-part of the electron diffraction pattern is shown in Figure 2b (left). In addition to the bright spot at the center caused by the direct electron beam irradiation, the diffraction pattern is mainly composed of a set of parallel diffracted layer lines which are separated by certain distances from the equatorial layer line at the center. By layer line distance analysis based on a novel concept of intrinsic layer line spacing,[9] the diffraction pattern has been indexed and the chiral indices of the SWCNT were determined to be (16,11) with the tube diameter of 1.84 nm. A simulated electron diffraction pattern of the (16,11) nanotube is given in Figure 2b (right) which is in good agreement with the experimental pattern (left).

In addition to the Raman features from SWCNT, the Raman bands related to the vibrational modes of fullerenes are also observed at 1465 and 264 cm^{-1}. Since no Raman analysis has been done on a NanoBud structure before, to understand the above Raman features from NanoBuds, we enlighten our study with the peapods structure, where fullerenes are encapsulated inside the SWCNT. It is known that for the fullerenes that many Raman-active modes are measurable at ambient condition.[10,11] However, for the structure combination of fullerenes and SWCNTs, such as peapods, because of the high intensity of Raman modes from SWCNTs, the Raman-active modes of fullerenes are difficult to detect; moreover, the mode intensity depends on the excitation energy and temperature.[12–15] In the case of C_{60} peapods, the most prominent mode is the pentagonal pinch mode $A_g(2)$ located in the range of 1440−1480 cm^{-1},[14–16] which is often used as a probe to detect C_{60} inside the nanotube. The excitation profiles of $A_g(2)$ mode for C_{60} peapod reveal one maximum at 2.5 eV.[17,18] When excited with the green laser at about 2.34 eV, the $A_g(2)$ mode becomes much weaker.[16,18,19] This case is similar to the C_{70} peapods, where

there are weak but clear peaks at 1446 and 1465 cm^{-1} at excitation energy around 2.38 eV.[19] In this work, at ambient condition with the excitation energy of 2.33 eV, the Raman peaks in the range of 1440−1480 cm^{-1} are quite clear (inset of Figure 2). They are associated with the typical vibrational modes of fullerenes in intrinsic presence of the CNT as discussed above. Additionally, a relatively weak peak at 264 cm^{-1} is also observed in the spectrum (inset of Figure 2). In comparison to preceding studies on materials formed by nanotubes and fullerenes as parent materials (peapods),[13] the presence of this peak suggests the presence of fullerenes on the SWCNT. The simultaneous observation of SWCNT and fullerenes in the Raman spectrum implicitly shows the presence of the NanoBud structure, which is once again confirmed with the HRTEM results (Figure 1d).

In summary, NanoBuds collected downstream of the reactor on a TEM grid were investigated by Raman spectroscopy in combination with TEM. The Raman studies of the single NanoBud structure provided for the first time the evidence of the simultaneous presence of SWCNT and fullerenes. The TEM and ED investigations on the same NanoBuds are in good agreement with Raman results, which confirmed the Raman measurement interpretation of the SWCNT chirality assignment and the presence of fullerenes on the surface of the SWCNT.

Supporting Information Available: Complete ref 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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