The local study of a nanoBud structure

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We studied a NanoBud structure in a local-scale using high resolution transmission electron microscopy (HRTEM), scanning tunnelling microscopy (STM) and Raman spectroscopy. The HRTEM images show fullerenes on the outer surface of a single-walled carbon nanotube (SWCNT) and the bonding between the fullerenes and SWCNT were examined by STM measurement, in which the fullerene attachment was stable against high bias imaging. We were also able to perform Raman measurement on a NanoBud structure. Characteristic features of the individual SWCNT, assigned as \( (16,11) \), and fullerenes were observed in the vibrational spectrum. The G band and the radial breathing mode (RBM) of SWCNTs as well as an additional feature at \( 1460 \text{ cm}^{-1} \) were clearly presented simultaneously, which indicate the NanoBud structure.

1 Introduction

New forms of carbon such as fullerenes and single-walled carbon nanotubes have attracted a great interest of scientists for many years due to their remarkable physical and chemical properties \([1, 2]\). A novel hybrid nanostructure, in which fullerenes are covalently bonded to the outer surface of SWCNTs, termed NanoBuds, was firstly observed by HRTEM images in our group and further investigated by means of Raman spectroscopy \([3, 4]\). This new material showed high cold electron field emission efficiency. It is expected that this novel material possesses many other advantageous properties. Taking into account higher reactivity of fullerenes compared to SWCNTs, this hybrid material may open new avenues for functionalization through chemical modification. The attached fullerene molecules could be used as molecular anchors to prevent slipping of SWCNTs in composites, thus improving the composite’s mechanical properties. Owing to the charge transport between SWCNTs and functionalizing fullerenes, both electrical and optical properties of the material can be tuned. The ability to directly synthesize SWCNTs having distinct regions with different electronic properties is of importance for many applications, including memory devices, decoders and tuneable quantum dots \([3]\).

In this paper, the NanoBud structure was further characterized at full local-scale study by using TEM, STM and Raman spectroscopy.

2 Experiment

The experimental method of continuous synthesis of the NanoBud samples was based on ferrocene vapor decomposition in a CO atmosphere \([5]\). The catalyst precursor was vaporized by passing ambient temperature CO (with a flow rate of \( 300 \text{ cm}^3/\text{min} \)) through a cartridge filled with ferrocene powder \([6]\). The flow containing ferrocene vapour was then introduced into the high temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with additional CO (\( 100 \text{ cm}^3/\text{min} \)).

The key parameter required for the NanoBud synthesis was experimentally found to be the presence of trace concentrations of H\(_2\)O vapour or CO\(_2\) as etching agents. The CO\(_2\) and H\(_2\)O vapour were introduced together with the
carbon source via a mass flow controller. The optimum reagent concentrations were found between 45 and 245 ppm for water and between 2000 and 6000 ppm for CO$_2$ [3].

The NanoBuds samples used in this study were produced at 900 °C with 2000 ppm of CO$_2$ and 100 ppm of H$_2$O gas concentration, respectively. The products were collected downstream of the reactor on the indexed TEM grids using an electrostatic precipitator [7]. The as-obtained products on the TEM grids were directly investigated with the TEM (Philips CM200 FEG) and Raman spectrometer (Wintech Alpha-300). The room-temperature Raman spectra were performed using a frequency doubled Nd:YAG green laser (λ = 532.25 nm) and Olympus 100× air objective. Once the CNT is in resonance with the laser energy, the full Raman spectra were 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). For STM study, the raw soot of NanoBuds sample were sonicated briefly in dichloromethane prior to being cast on freshly grown Au(111) substrates. High resolution topographic STM images were obtained in ambient conditions using Nanoscope IIIa system.

3 Results and discussion

Figure 1 displays a typical example of the NanoBuds morphology. The TEM images show that the sample contains SWCNT bundles with diameters below 20 nm and length up to several micrometers. The high resolution TEM images (Figs. 1(c) and (d)) revealed the presence of fullerenes on the surface of the CNTs. Their concentration depends strongly on the sample growth parameters. For this particular study we used samples that were fabricated at 900 °C with 2000 ppm of CO$_2$ and 100 ppm of H$_2$O gas concentration. These growth parameters favour high concentration of fullerenes on the surface of SWCNTs, thereby enhancing the signal intensity of the fullerenes vibrational modes.

For direct real space characterization, we have performed STM measurements on an individual NanoBud structure. Figure 2 shows a typical STM topographic image of the NanoBud on a chiral SWCNT. It is worth noting that the image we present here has not been processed in anyway. The NanoBud appears as a round protrusion which is attached to the nanotube wall. The NanoBud attachment was stable against high bias imaging and continuous room temperature scans, thereby confirming the strong attachment to the nanotube wall.

To utilize the local-scale analysis of the hybrid nanosstructure that has the SWCNT and fullerenes as parent structures by Raman spectroscopy, we focused on a single NanoBud structure which is shown in Fig. 3(a). On this freestanding tube, we firstly conducted electron diffraction experiments. The electron diffraction pattern is shown in Fig. 3(b). 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 [8], 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.

The Raman spectrum from the same NanoBud structure was shown in Fig. 3. As expected for the individual SWCNT, a single narrow radial breathing mode (RBM) was observed at 133 cm$^{-1}$. Based on the equation...
Figure 3 (a) A high-resolution TEM image and (b) ED pattern of the NanoBud structure. The SWCNT was assigned as (16,11). Raman spectrum of the NanoBud structure (c) RBM and (d) G modes of (16,11) SWCNT are presented and the arrows indicated the fullerene features at 264 and 1460 cm$^{-1}$ ($E_{\text{laser}} = 2.33$ eV).

$\omega = 223/d + 10$ [9], 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 [10, 11], this SWCNT can be assigned as the (16,11) semiconducting nanotube, which is in good agreement with ED results. The high $I_G/I_D$ ratio (~30) indicates the low defect formation in the SWCNT. At this point it is worth noting that the presence of this D band suggests the covalent bonding that attaches fullerenes to the surface of SWCNT, since it is known that even a low amount of exohedral bonded carbon leads to an increase of the intensity of the D-bands.

Besides the Raman features from the SWCNT, the Raman features related to the vibrational modes of fullerenes are also observed at around 1460 and 264 cm$^{-1}$. Since the NanoBud structure was not investigated by Raman spectroscopy 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 even a low amount of exohedral bonded carbon leads to an increase of the intensity of the D-bands.

4 Conclusions The NanoBud structure was investigated by TEM, STM and Raman spectroscopy. The TEM and STM results showed the NanoBud structure i.e. the fullerenes were bonded to the surface of a SWCNT. Combining with the TEM experiment, the single NanoBud structure was also detected by Raman spectroscopy. The characteristic features of both SWCNT and fullerenes were shown in the Raman spectrum simultaneously using a 2.33eV excitation. The interpretation of the SWCNT chirality assignment and NanoBud structure from Raman results are in good agreement with the measurements of the HRTEM and ED presenting the NanoBud structure with (16,11) chirality SWCNT.

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References


