Diameter-selective encapsulation of metallocenes in single-walled carbon nanotubes

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Encapsulation of organic molecules in carbon nanotubes has opened a new route for the fabrication of hybrid nanostructures. Here we show that diameter-selective encapsulation of two metallocene compounds bis(cyclopentadienyl) cobalt and bis(ethylcyclopentadienyl) cobalt has been observed in single-walled carbon nanotubes. In particular, bis(cyclopentadienyl) cobalt is observed to fill only nanotubes of one specific diameter. Electron transfer from the cobalt ions to the nanotubes has been directly observed through a change in the charge state of the encapsulated molecules. The filling of the tubes is found to induce a red-shift of the photoluminescence emission, which is attributed to the formation of localized impurity states below the conduction band of the nanotubes.

The encapsulation of molecules inside carbon nanotubes has opened a new route for engineering the electronic properties of the nanotubes[1,2]. In particular, the production of air-stable n-type single-walled carbon nanotubes (SWCNTs) by the encapsulation of organic molecules inside the tubes has been reported[3], and the potential for doping using a variety of different molecules has been examined theoretically[4]. Recent studies of scanning tunnelling spectroscopy (STS) have shown that fullerenes or metallofullerenes encapsulated in semiconducting SWCNTs significantly modify the local electronic structures of the tubes[5,6]. Although no shift in intrinsic optical bandgap has previously been reported, these peapod-like materials still raise the exciting possibility of producing a nanomaterial with a tunable structure that can be tailored to a specific electronic functionality. In this report, we have inserted two organometallic compounds bis(cyclopentadienyl) cobalt ($CoCp_2$ or cobaltocene) and bis(ethylcyclopentadienyl) cobalt ($Co(EtCp)_2$) into SWCNTs. We show that highly diameter-selective encapsulation occurs and that this leads to large red shifts in the band-edge emission. Encapsulation of these molecules introduces localized impurity (donor) states below the conduction band, which significantly modify both the emission and absorption processes.

We expect that there will be a threshold for the nanotube size before filling with specific molecules can occur. The van der Waals surface of $CoCp_2$ can be approximated by a cylinder of 0.65 nm in diameter and 0.69 nm in length, calculated from bond lengths and van der Waals radii of the atoms constituting $CoCp_2$ (ref. 7). As the van der Waals radius of an sp_2-bonded carbon in the nanotube walls is ~0.15 nm, it is expected that the smallest tube diameter capable of being filled without straining the tubes would be around 0.95 nm (= 0.65 nm + 2 × 0.15 nm). Because the ethyl substituents are flexible in conformations, the critical diameter for $Co(EtCp)_2$ filling is expected to be similar to that for $CoCp_2$.

In Fig. 1a,b are TEM micrographs of selected individual nanotubes showing the encapsulation of $CoCp_2$ and $Co(EtCp)_2$, respectively, and Fig. 1c shows the structure diagrams of $CoCp_2$ and $Co(EtCp)_2$. The TEM shows clear evidence for the $CoCp_2$
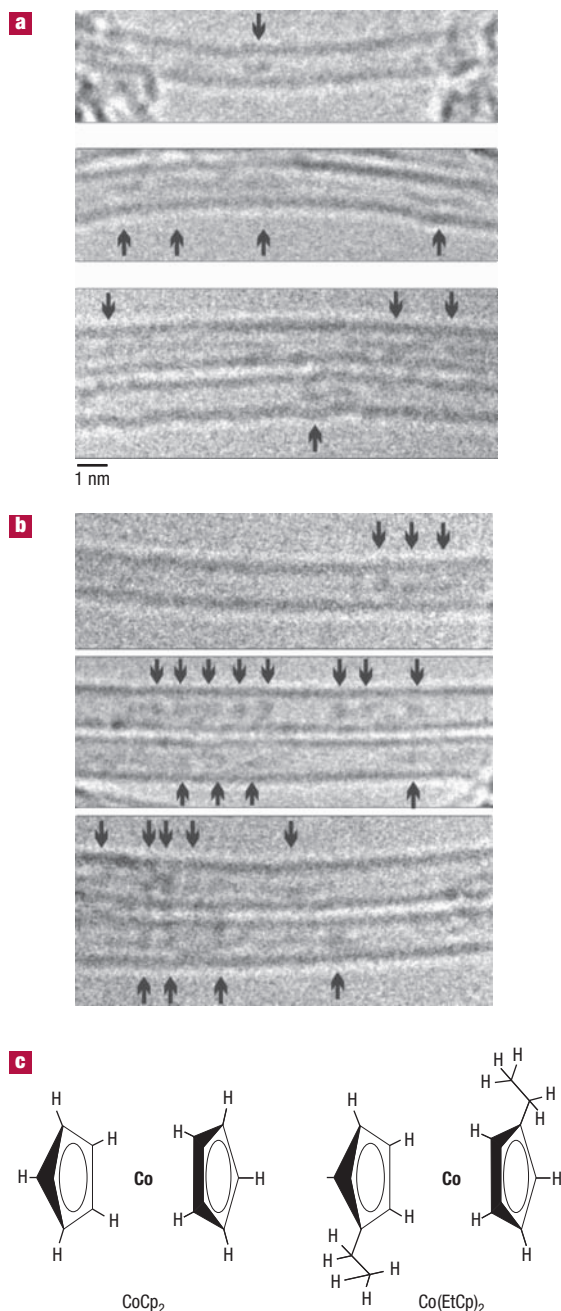
Figure 1 TEM micrographs of $CoCp_2$ and $Co(EtCp)_2$ molecules encapsulated in carbon nanotubes. **a**, $CoCp_2$ molecules in a nanotube, as indicated by the arrows. **b**, $Co(EtCp)_2$ molecules in a nanotube. **c**, Chemical structures of $CoCp_2$ and $Co(EtCp)_2$.
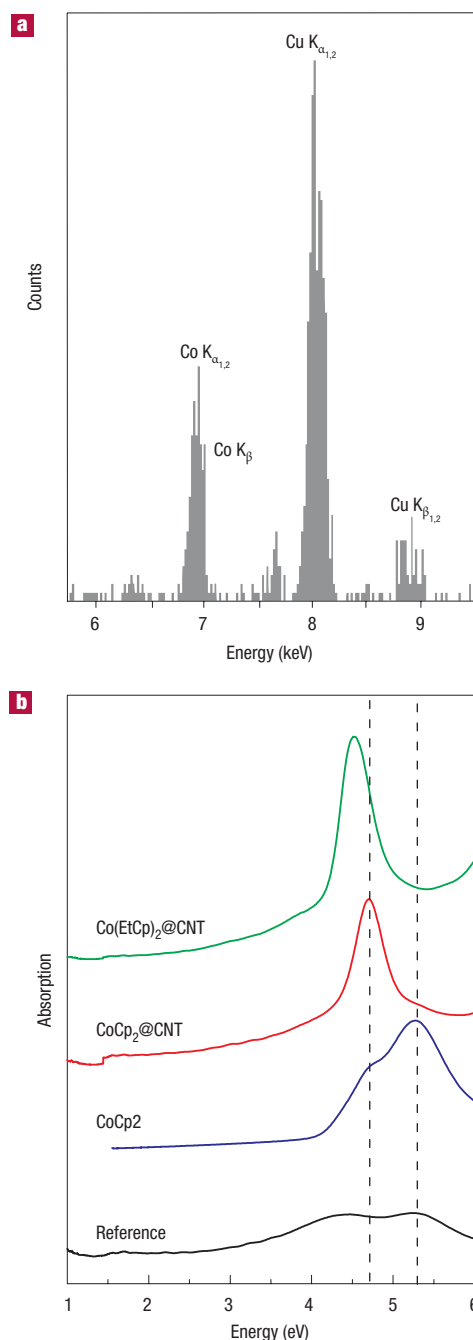
Figure 2 EDX and absorption spectra showing the encapsulation of $CoCp_2$ and $Co(EtCp)_2$ molecules. **a**, EDX spectrum of an isolated bundle of $Co(EtCp)_2$@CNT taken with a 10-nm e-beam probe. **b**, UV-visible absorption spectra of $CoCp_2$, $CoCp_2$@CNT, $Co(EtCp)_2$@CNT and the reference sample in a 1-wt% SDS–D_2O solution. The dashed lines mark the positions of the strong $CoCp_2$ absorption at 5.277 eV and the ($CoCp_2^+$) absorption at 4.706 eV.

encapsulation only in a tube of diameter ~1 nm, whereas for $Co(EtCp)_2$ encapsulation is observed in a range of tube diameters greater than ~1 nm. The distribution and shape of individual molecules cannot be clearly identified due to a rapid molecular motion or degradation of the metallocenes in the TEM beam under the imaging conditions. Figure 2a shows the EDX spectrum taken for $CoCp_2$@CNT structures. It confirms the existence of cobalt within the SWCNTs as both lines CoK_α at 6.93 keV and CoK_β at 7.65 keV are detected (the copper lines are due to the specimen holder). Figure 2b compares the absorption features of $CoCp_2$, $CoCp_2$@CNT,

$Co(EtCp)_2$@CNT and the reference sample. Two very strong absorption bands for $CoCp_2$ at 5.277 eV and 4.788 eV are assigned to the metal-to-ligand (M–L, $e_{1g} \rightarrow e_{2u}$) and ligand-to-metal (L–M, $e_{1u} \rightarrow e_{1g}$) charge-transfer transitions respectively[8]. The smearing of the M–L absorption and a slight shift of the L–M absorption to a lower energy (4.706 eV) for CoCp2@CNT indicates the formation

Table 1 Photoluminescence spectral data and assignments. The peak numbering follows Fig 3. The chiral indices n, m and quantum number q are from previous literature assignments[16,21]. The peak energies were deduced using multiple peak fitting analysis.

Peak	E_g (eV) Ref.	ΔE_g* (meV) Co(EtCp)$_2$	ΔE_g* (meV) CoCp$_2$	n	m	q	Diameter[†] (nm)
1	1.195	−3	3	7	5	−1	0.827
2	1.163	0	4	10	2	−1	0.883
4	1.092	−4	4	7	6	1	0.893
3	1.112	−5	3	9	4	−1	0.914
7	0.992	−18	−19	10	3	1	0.935
5	1.046	−11	1	8	6	−1	0.964
9	1.046	−24	0	12	1	−1	0.993
10	1.018	−20	−2	11	3	−1	1.012
12[‡]	0.976	−12	2	8	7	1	1.018
8	0.900	§	0	12	2	1	1.040
6	1.021	−25	2	10	5	−1	1.049
11	0.984	−27	−1	10	5	−1	1.049

*ΔE_g is the shift relative to the peak energies of the reference sample in column 2.
[†]calculated from n and m assuming a lattice constant for graphite of $a = 0.249$ nm.
[‡]Excited by 720 nm laser.
§Unpronounced peak.

of cobaltocenium ions[9] (CoCp$_2^+$). This confirms the presence of the CoCp$_2$ molecule in the nanotubes and suggests the oxidation state of almost all of the cobalt ions has changed from Co(II) to Co(III), suggesting the occurrence of substantial electron transfer from the CoCp$_2$ to the nanotubes.

Figure 3a,b shows the bandgap photoluminescence from the reference, CoCp$_2$- and Co(EtCp)$_2$-filled tubes, which have been excited with two different wavelengths to enable us to distinguish the emission from different tubes. This shows that relative to the unfilled reference sample there is a relatively large red-shift for the longer wavelength tubes in case of Co(EtCp)$_2$ filling. However, only one peak of those that are present in the HiPCO tubes (peak 7) shows a significant red-shift for CoCp$_2$ filling. Table 1 lists the tube characteristics in order of tube diameter, and shows the energy shift relative to the reference sample produced by filling with Co(EtCp)$_2$ (or CoCp$_2$) as deduced from the spectra shown in Fig. 3. In the case of Co(EtCp)$_2$ filling, the bandgap shifts are divided into two groups: (i) large shifts of the order of 11–27 meV for nanotubes with diameters above 0.92 nm and (ii) small shifts that lie within the fitting error bars of ±2 meV for nanotubes with diameters below 0.92 nm. The two groups of peaks are shown separated by a vertical line in Fig. 3. The observed threshold diameter of 0.92 nm is in good agreement with the predicted threshold value of ~0.95 nm for unstrained filling. This confirms the qualitative conclusion drawn from the TEM pictures, which suggested that Co(EtCp)$_2$ is preferentially encapsulated into SWCNT with diameters above a

threshold value and that the filling causes an emission shift for these nanotubes. By contrast, the CoCp$_2$-encapsulation results in only one detectable peak shift corresponding to the nanotube with a diameter of 0.935 nm, indicating a high selectivity for encapsulation into nanotubes with only a very small range of diameters.

Figure 4a displays high-resolution optical absorption spectra for Co(EtCp)$_2$@CNT, CoCp$_2$@CNT, the reference sample and the as-received SWCNTs in aqueous solutions. The features in the 0.8–1.55 eV range belong to the first van Hove transitions (E_{11}) and the peaks in the range of 1.38–2.25 eV are assigned to the second order van Hove transitions (E_{22}) for semiconducting nanotubes. The data show two main phenomena. First, they demonstrate the same diameter specificity observed in the photoluminescence, with only a single peak shifting for the CoCp$_2$@CNT, and a threshold for the observation of a (less well resolved) shift for the Co(EtCp)$_2$@CNT. Second, there is a clear enhancement of the absorption strength of the lower energy peaks for the E_{11} regime only, which is the signature of a nanotube distribution where the chemical potential has been raised into the region of the bandgap[10,11]. It is known that nanotubes can be strongly p-doped by oxygen under ambient conditions[12,13]. The absorption spectrum of the reference sample is similar to that of the as-received nanotubes, showing that the oxygen-doping during our thermal treatment for cap-opening is not significantly increased over that produced in the purification of the original HiPCO nanotubes. The relatively noticeable intensity enhancement of the E_{11} absorptions below 1.0 eV for both Co(EtCp)$_2$@CNT and CoCp$_2$@CNT indicates
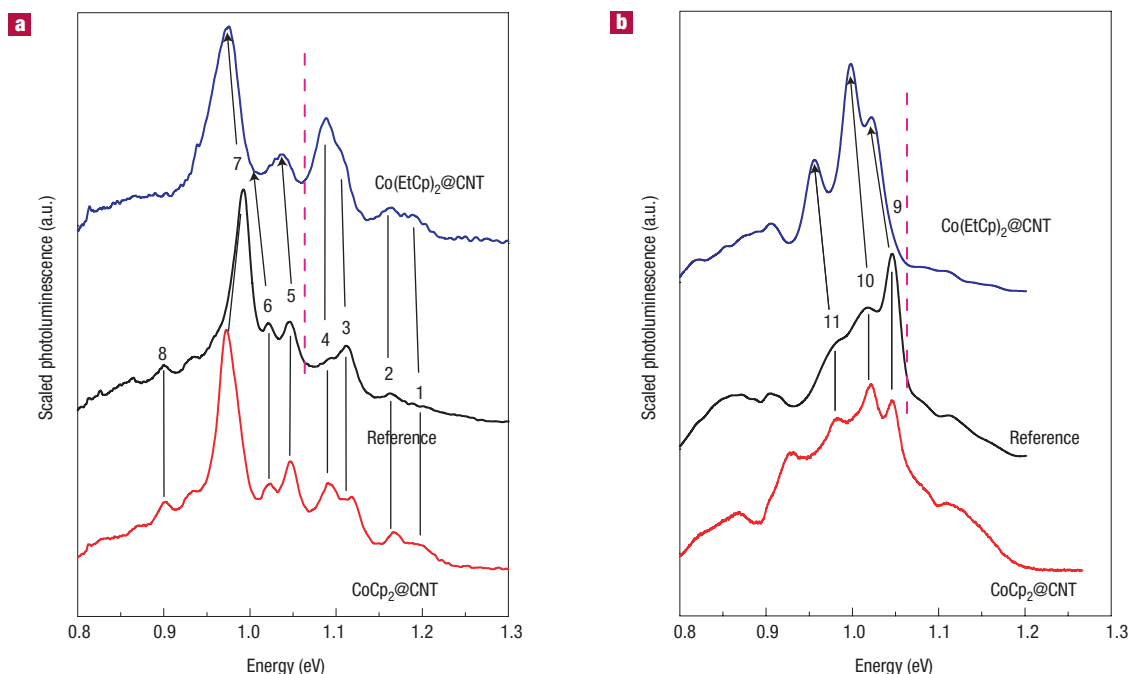
Figure 3 Comparison of photoluminescence from CoCp₂@CNT, Co(EtCp)₂@CNT and the reference sample. Samples excited with **a**, 633 nm and **b**, 810 nm lasers. The dotted line at 1.06 eV indicates the filling threshold for Co(EtCp)₂. (Identifiable peaks are numbered in order of bandgap energy.) Data for the numbered peaks are given in Table 1.
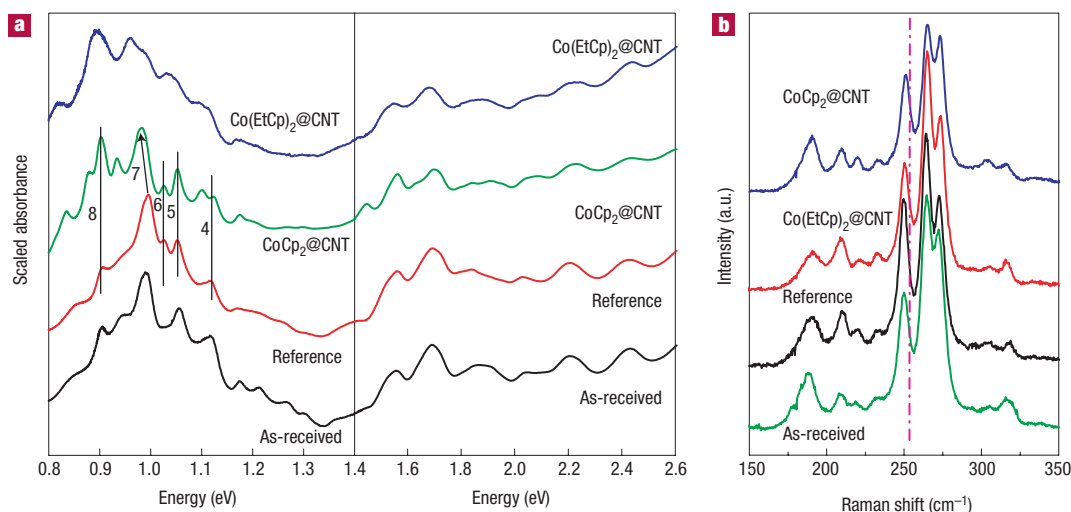

Figure 4 Comparison of absorption and Raman spectra. a, UV-visible-near infrared absorption spectra for Co(EtCp)₂@CNT, CoCp₂@CNT, the reference sample and the as-received SWCNTs in aqueous solutions. **b**, Raman measurements of the radial breathing mode for Co(EtCp)₂@CNT, CoCp₂@CNT, the reference and the as-received SWCNTs excited by a 514.5 nm laser. The vertical dash-dot line indicates the calculated Raman frequency from a nanotube with 0.92 nm diameter.

that the filling procedure is a process that adds electrons to the tubes, thus compensating the p-type doping effect of the oxygen and corroborating the change in ionization state of the cobaltocene shown in Fig. 2. The fact that the low-energy absorption in Fig. 4 has been enhanced in the CoCp₂@CNT shows, however, that some de-doping occurs even for nanotubes that do not have encapsulated cobaltocene. It is difficult to measure the exact filling fraction for the different diameters of tubes, however we estimate the total weight ratio for

encapsulated molecules to the total SWCNT to be approximately 0.23:1 for Co(EtCp)₂@CNT and 0.03:1 for CoCp₂@CNT, based on a quantitative analysis of the absorption spectra in Fig. 2b, which seems consistent with the images in Fig. 1.

One striking feature of our results is that all of the encapsulation-induced shifts in emission energy are of a comparable magnitude and the same sign. This suggests that the mechanism for the red-shifts is essentially perturbative and might be induced by the presence of

the cobaltocenium ions acting as shallow donors, which then cause red shifts on an energy scale comparable to the exciton binding energies. For the tubes studied here[14–16], these energies are calculated to be of the order of 100–300 meV with corresponding exciton sizes of a few nanometres, which are comparable to the spacing of the cobaltocenium ions. In conventional semiconductors, transitions involving impurity-bound excitons or direct donor–acceptor pair recombination are typically red-shifted by the order of 10–30% of the exciton binding energies from the free exciton transitions[17]. Our observed values of 20 meV are thus consistent with these values. This picture is also supported directly by the density functional theory reported elsewhere[4], which suggested that the bottom of the partially filled γ-band of $CoCp_2$ lies within 0.1 eV of the conduction band edge of a (16,0) nanotube ($E_g = 0.86$ eV).

The effects of local elastic strain and charge transfer from encapsulated metallofullerenes have been proposed to explain the much larger bandgap changes deduced by scanning probe microscopy in encapsulated metallofullerene systems[6]. The measurements reported here suggest that strain effects are not important as we observe that the bandgaps of all of the filled tubes consistently shift to lower energy by a similar amount, whereas strain is known to produce both positive and negative shifts varying in magnitude and sign with the chiral vector[18,19]. Raman measurements of radial breathing mode shown in Fig. 4b suggest that there are no large strains present and the diameters and size distribution are virtually unchanged by the process of $Co(EtCp)_2$ or $CoCp_2$ encapsulation.

We suggest that the origin of the very different diameter-selectivity may be explained by the effects of molecular size. $CoCp_2$ sublimes under our nanotube-filling condition, so that the $CoCp_2$ molecules enter any SWCNT with diameters larger than 0.92 nm. Only those nanotubes that interact strongly with $CoCp_2$ can irreversibly trap the $CoCp_2$. It has been calculated that absorption of $CoCp_2$ in a relatively wide (16,0)-nanotube ($d = 1.27$ nm) is only slightly exothermic[4], which implies the $CoCp_2$ can be easily desorbed from wider nanotubes during the filling process. We expect that only SWCNT with a good geometrical fit (diameter ~0.92 nm) to the size of $CoCp_2$ will have sufficiently strong interaction to permanently trap the molecule. In contrast, the flexible ethyl chains make the $Co(EtCp)_2$ less conformationally rigid enabling a stronger van der Waals interaction to occur in larger diameter nanotubes.

The induced red shift in the emission and absorption energies of the carbon nanotubes due to formation of cobaltocenium ions suggests that the role of excitons in the emission process is significant. In addition the filling of only one specific nanotube species suggests that it may be possible to produce a highly selective doping process, which will enable nanotube selection by using the magnetic properties of the encapsulated cobalt. Further development of ferromagnetic interactions might be achieved through encapsulation of the cobaltocene to form nanostructures with new magnetic properties.

METHODS

SWCNTs (from Carbon Nanotechnologies) synthesized by the high-pressure CO conversion (HiPCO) method were oxidized in air at 360 °C for 30 min followed by 375 °C for 10 min. The thermal treatment opened the nanotube caps and partly removed amorphous carbon from the surface of the SWCNT. Some of the oxidized material was left as an unfilled reference sample. The rest was mixed with an excess of $CoCp_2$ (or $Co(EtCp)_2$) under a nitrogen atmosphere and placed in a quartz tube, sealed in a vacuum of 10^{-3} torr and heated at 100 °C for three days, followed by dispersion in a 1:1 mixture of toluene and methanol with a mild sonication to

dissolve unencapsulated $CoCp_2$ (or $Co(EtCp)_2$). The mixtures were then filtered and washed with toluene and methanol until the filtrate was colourless. The $CoCp_2$-filled nanotubes ($CoCp_2$@CNT) or $Co(EtCp)_2$-filled nanotubes ($Co(EtCp)_2$@CNT) were then collected from the filter as a black powder. Aqueous sodium dodecyl sulphate (SDS) suspensions of the reference nanotubes, $CoCp_2$@CNT and $Co(EtCp)_2$@CNT were used for photoluminescence and absorption studies and were prepared using sonication and ultracentrifugation following the method suggested previously[20]. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy measurements were performed in JEOL4000EX $L\alpha B_6$ and JEOL JEM-3000F field-emission-gun TEMs, equipped with a super-atmospheric thin-window X-ray detector. The absorption spectra of the SWCNT solutions were measured using a Perkin-Elmer UV-Vis-NIR spectrophotometer (Lambda 9). The photoluminescence was measured by inserting a single excite fibre and six collecting fibres directly into the sample solutions[16]. The photoluminescence was excited with 633, 720 and 810 nm excitation wavelengths as variation of the excitation wavelength induces preferential luminescence from specific semiconducting nanotubes by direct excitation into the second van Hove electronic transition[21]. For Raman spectroscopy, a drop of methanol–SWCNTs suspension was placed onto Si substrates and dried at room temperature. Raman measurements were performed at 300 K in a back-scattering geometry using an Ar^+ laser at 514.5 nm for excitation (power density on sample: 8×10^5 W m^{-2}) and a Jobin-Yvon T64000 triple grating spectrometer with a nitrogen-cooled multichannel CCD detector.

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Competing financial interests

The authors declare that they have no competing financial interests.