A combined photoemission and \textit{ab initio} study of the electronic structure of (6,4)/(6,5) enriched single wall carbon nanotubes

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Received 2 June 2010, accepted 26 July 2010
Published online 13 September 2010

\textbf{Keywords} photoemission spectroscopy, single wall carbon nanotubes

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Due to the growing number of applications of small diameter single wall carbon nanotubes (SWCNTs) in opto-electronics and biological imaging, there is a strong need for a better understanding of their electronic properties. Because (6,5) tubes with a diameter of 0.75 nm are currently the strongest enriched in the CoMoCat synthesis process, they are one of the most studied carbon nanotubes. However, there is still a lack of knowledge on the electronic properties of these tubes. In this paper, we report on a detailed analysis of the electronic structure of (6,4)/(6,5) enriched nanotubes with a combined experimental and theoretical approach. From photoemission the detailed C1s and valence band response of these narrow diameter tubes is studied. The observed electronic structure is in sound agreement with state of the art \textit{ab initio} calculations using density functional theory.

\section{Introduction}

The intriguing properties of small diameter carbon nanotubes make them fascinating topics for many researchers. Whereas the basics of the physical properties of single wall carbon nanotubes (SWCNT) are understood [1], the increasing curvature for smaller diameter tubes poses new challenges. Among these, in particular (6,5) tubes with a diameter of 0.75 nm are currently the most studied SWCNTs because of their exceptional enrichment established in the CoMoCat synthesis process [2]. Their unique optical and luminescence response [3], the special property of fluorescing in a region of the near infrared [4], where human tissue and biological fluids are particularly transparent for their emission, makes them very useful for biological imaging as well as for biosensing [5–7].

Several methods have been developed and optimized to synthesize such small diameter tubes with a mean diameter below 0.8 nm. Kitiyanan et al. [2] successfully controlled the production of SWCNTs by catalytic decomposition of CO on bimetallic Co–Mo catalysts yielding an enrichment of especially (6,4) and (6,5) tubes. On the other hand, a pattern of (6,5) and (6,4) tubes have been synthesized via the growth of double wall carbon nanotubes (DWCNTs) [8–10]. This nanochemical reaction inside SWCNTs was achieved by high temperature annealing of peapods (C\textsubscript{60} @ SWCNTs) without any further catalyst.

In order to separate SWCNTs in mainly one (n,m) tube type, several processes have been developed. In recent years, the main procedures involve DNA wrapping [11–13], chromatographic separation [13, 14] and density gradient ultracentrifugation (DGU) [15]. In particular (6,5) SWCNTs have been both separated successfully and analyzed in detail.
regarding the yield with photoluminescence spectroscopy [11, 13, 16, 17]. However, for most of these samples the direct observation of their electronic properties by surface science techniques was complicated by the presence of byproducts from the used surfactant and/or by the low yield of the separation process. Recently, purified samples without remaining surfactant of (6,4)/(6,5) chirality enrichment have been available as bulk mats of SWCNTs (a so-called bucky paper) [18].

Several theoretical approaches have been used to analyze the electronic structure of narrow diameter tubes. Semi-empirical tight-binding calculations, which work very well for large diameter SWCNTs [1, 19], have to be extended since they neglect the curvature of these small diameter tubes. Particularly for small diameter tubes, the carbon–carbon bonds on the curved nanotube surface become inequivalent because π-orbitals, being parallel in graphite, are no longer parallel on a curved surface. This involves a change in overlap between neighbouring π-orbitals. This was partly solved by Popov [20] who studied the effect of curvature on the structure, electronic and optical properties of isolated SWCNTs within a symmetry-adapted non-orthogonal tight binding model using 2s and 2p electrons of carbon. However, the exact values for the transition energies are still not reproduced sufficiently well. Ab initio calculations of highly chiral diameter SWCNTs have until recently been too computationally expensive since the unit cell of the (6,5) and (6,4) tubes contains hundreds of atoms [21]. Hence, to date there is only one result from Chang et al. [22] utilizing a symmetry adapted local density approximation (LDA) ab initio approach to calculate such tubes with large unit cells. These results were applied to calculate the optical matrix elements and exciton binding energies for (6,5) tubes in comparison to two photon experiments [23].

In this paper we compare experimental and theoretical data of the electronic structure of (6,4)/(6,5) enriched nanotubes. Photoemission reveals the detailed C1s and valence band response of these narrow diameter tubes. This observed electronic structure is in sound agreement with our new extensive state of the art ab initio calculations using density functional theory (DFT).

2 Methods The experiments were carried out on a CoMoCAT sample, enriched with (6,5) SWCNTs by DGU method [15]. After filtering, the obtained film was transferred onto a copper sample holder fixed by a Ta foil and annealed at 1000 K in a UHV preparation chamber followed by a subsequent transfer to a variable temperature He cryostat attached to the measurement chamber. The base pressure was always below 2 × 10−10 mbar. The PES experiments were performed at beamline UE 52 PGM at Bessy II, which has a resolving power (E/ΔE) of 4 × 104 [24]. For PES a hemispherical photoelectron energy analyzer SCIENTA SES 4000, with the energy resolution set to 10 meV, was used. All spectra were recorded at 15 K with an effective energy resolution better than 30 meV. The excitation energies were calibrated by the Fermi edge of clean Au films. The enrichment was checked by resonance Raman optical absorption and luminescence spectroscopy taking into account the corresponding different cross sections for the individual tubes. We found that the enrichment of (6,4) and (6,5) tubes, which are roughly of equal concentration in the bulk sample, is about 80% of all thin diameter nanotubes [25]. In this report we also determined the main fractions of the 20% other tubes which are of (7,5), (8,4) and (9,1) chirality. For comparison, we also show results on a sample with large diameter semiconducting SWCNTs from a previous report [26], with a mean diameter of 1.37 nm. This sample is referred to as SC-SWCNT.

All calculations have been performed using the real-space DFT code GPAW [27], based on the projector-augmented wave method, with the PBE exchange-correlation (xc)-functional [28]. A grid spacing of 0.2 Å was used to represent the electron density and wavefunctions, and all structures were relaxed until a maximum force below 0.03 eV/Å was obtained. For the unit cells obtained after minimization a Γ-point sampling of the Brillouin zone was sufficient to describe the equilibrium electron density ((6,4) SWNT dimensions: 18.618 Å × 20.0 Å × 20.0 Å (6,5) SWNT dimensions: 40.747 Å × 20.0 Å × 20.0 Å). However, to describe the density of states a 50 k-point sampling of the Brillouin zone along the nanotube axis was employed with the equilibrium electron density kept fixed.

3 Results and discussion At first, a survey scan is carried out in order to check for the purity of this sample. In the left panel of Fig. 1 this survey reveals only a very small contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfactants and catalysts. From the C1s to O1s ratio we detected an contamination from adsorbates and remaining surfac...
The composition of the sample is analyzed with different optical techniques [25]. The C1s photoemission response of this (6,4)/(6,5) enriched sample is measured with a photon excitation energy of 400 eV at a temperature of 35 K and shown in the right panel of Fig. 1 as the green line. This measurement is compared with a previous measurement on purely semiconducting nanotubes with 1.37 nm mean diameter [26], represented by a navy dashed curve. The overall shape is similar. A detailed line shape analysis is made in Fig. 2, where the C1s response is shown on a larger scale. The inset of Fig. 2 shows the C1s response of the (6,4)/(6,5) enriched sample in comparison with purely semiconducting SWCNTs.

98%. The composition of the sample is analyzed with different optical techniques [25]. The C1s photoemission response of this (6,4)/(6,5) enriched sample is measured with a photon excitation energy of 400 eV at a temperature of 35 K and shown in the right panel of Fig. 1 as the green line. This measurement is compared with a previous measurement on purely semiconducting nanotubes with 1.37 nm mean diameter [26], represented by a navy dashed curve. The overall shape is similar. A detailed line shape analysis is made in Fig. 2, where the C1s response is shown on a larger scale. The inset of Fig. 2 shows the C1s response of the (6,4)/(6,5) enriched sample in comparison with purely semiconducting SWCNTs in an expanded range around the C1s binding energy. The maximum represents the binding energy and is 284.47 eV for the (6,4)/(6,5) enriched sample and 284.43 eV for the SC-SWCNT. This difference in binding energy of about 40 meV indicates that the binding energy value could be associated to the diameter and chirality. Both curves are characterized by a symmetric Voigtian curve. However, this graph clearly shows the remarkable difference in peak width between both samples. The full width at half maximum (FWHM) for the (6,4), (6,5) enriched sample is 0.46 eV compared to 0.29 eV for the SC-SWCNT and 0.32 eV for the well-known graphite. Consequently this big difference has triggered our attention and has lead us to find alternative explanations.

The shape of the C1s response, including the response from the plasmon satellites and the shake up structures, was carefully analyzed in Fig. 2. Using Voigtian lines and subtracting the Shirley background, we observe a very good agreement with three components for the main C1s line and three broad contributions for the shake up and the π and π + σ plasmon satellites. The three peaks at 284.42, 284.49 and 284.52 eV have a relative spectral weight of 44%, 20% and 36%, respectively. These results are in sound agreement with the (6,5) to (6,4) ratio of about 1:1 and the 80% enrichment factor of these chiralities determined in our optical experiments [25]. We assign the binding energy of 284.42 eV to the (6,4) tubes and the higher binding energy of 284.52 eV to the (6,5) tubes. The line width of these two components is 0.41 eV. The increased linewidth of about 1 eV of the 284.49 eV component can be related to the mixture of the different narrow diameter tubes with (7,5), (8,2) and (9,1) chirality as main contributions. The observed difference in binding energies seems to depend on the different chemical potentials. A first possibility is the larger bonding angle variation for narrow diameter tubes due to the strong curvature [29]. Surprisingly, the line width is significantly broader than for C_{60} which has a similar curvature and also only one sp^2 bonding environment. However, without changing the I_h symmetry of the fullerene cage when going from C_{60} to Dy_3N@C_{80} or Sc_3N@C_{80} [30, 31] the different sp^2 bonding environments in the C_{80} cage results in an C1s line width of 0.9 eV.

Figure 3 represents the photoemission spectrum of the valence band, measured with an excitation energy of 150 eV for the (6,4)/(6,5) enriched sample (green open circles). The inset is a wide range comparison with the SC-SWCNT with 1.37 nm mean diameter (navy open squares) [26]. The overall shape is very similar. However, close to the Fermi level distinct differences are observed. In order to analyze these details in the electronic structure of the π band, a high resolution close up of the valence band photoemission at low binding energies is shown in Fig. 3. The maximum in the DOS is observed around 3 eV and is the π peak, well known from the M point of graphene. In addition, a distinct fine structure in the DOS is observed which can be matched with previous results on metallic mixed [32, 33] and metallicity separated SWCNTs [26] with thick diameters assigned to van Hove singularities (VHS) in the DOS.

In order to identify this fine structure just below the Fermi level, the DOS of (6,4) and (6,5) SWCNTs were calculated. For previous samples, with a larger mean
diameter, a very good agreement with diameter cumulative 
tight-binding calculations was observed. As mentioned 
above such calculations fail here because of changes in the 
tight binding overlap due to the increased influence of 
the curvature for small diameter SWCNT. Therefore we 
performed state of the art ab initio calculations. In order to 
take into account the resolution broadening, a Gaussian 
convolution is then applied. Since the (6,4) and (6,5) tubes 
have a different chemical potential in comparison to the 
reference Fermi level of gold and since the actual value of 
the energy gap is underestimated in the DFT calculations, we 
shifted the calculated DOS by +0.18 eV for the (6,4) tubes 
and by −0.4 eV for the (6,5). As the PES lifetime is energy 
dependent and unknown in our samples, we did not apply any 
 further broadening of these calculated curves. The sum of 
these calculated, shifted and broadened DOS for the (6,4) and 
(6,5) SWCNT is plotted in purple. The agreement regarding 
the actual positions of the peaks in the experimental spectra 
is very good.

4 Summary We compared experimental and theoretical 
data of the electronic structure of (6,4)/(6,5) enriched 
nanotubes. With photoemission, the detailed C1s and 
valence band response of these narrow diameter tubes was 
observed. A careful analysis of the lineshape of the C1s 
revealed a different binding energy for (6,4) and (6,5) tubes. 
Most probably this is due to a different chemical potential. 
New extensive state of the art calculations using 
DFT were carried out for the DOS of the (6,4) and (6,5) tubes. 
These calculations are in qualitative agreement with 
the observed electronic structure.

Acknowledgements T. P. and K. DB acknowledge financial 
support from DFG projects PI 440 3/4/5. T. P. thanks the FWF 
P21333-N20 and H. S. the Leverhulme Trust for support through an 
early career fellowship and EPSRC through Portfolio Partnership 
We acknowledge European Community’s Seventh Framework 
Program (FP7/2007-2013) under grant agreement No. 226716.

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