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Probing quantized image-potential states at supported carbon nanotubes

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Abstract

Discrete image-potential states (ISs) are revealed at double-walled carbon nanotubes by means of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) in the distance–voltage $z(V)$ spectroscopy mode. The nanotubes are supported by flat Au(111) substrates. Due to the high sensitivity of the hot IS electrons to local variations of the surface potential, they can be considered as a sensitive probe to investigate interactions with the supporting substrate and impurities or defects at the nanotube surface. ISs provide information on the local electronic structure as well as on the electron dynamics at supported nanotubes.

(Some figures in this article are in colour only in the electronic version)

Image-potential states (ISs) are exotic electronic states that arise in the close vicinity of a surface due to confinement of electrons along the surface normal, by the crystal surface potential at one side and by the Coulomb image potential at the vacuum side [1, 2]. This confinement leads to the formation of discrete hydrogen-like Rydberg states with energies (with respect to the vacuum level) given by [1]

$$E_n = -0.85 \text{eV} \left(\frac{n+a}{n^2}\right)^2,$$

where $n$ is the principal quantum number and $a$ takes into account material-dependent deviations from the purely 1D hydrogen model. The high-energy electrons occupying ISs act as a two-dimensional (2D) free-electron-like gas that can move freely along the surface and that hence are sensitive to local variations of the surface potential due to, for example, local surface defects. ISs therefore provide an ideal playground for investigation of the electronic structure and dynamics of excited electrons at surfaces [3, 4]. While ISs formed at (flat) surfaces have been investigated intensively [3, 5–9], similar studies of ISs at nanostructures remain limited [4, 10–12]. Only recently, the existence of ISs at carbon nanotubes (CNTs)—cylindrical tubes consisting of one or more rolled-up graphite monolayers, i.e. graphene layers [13]—was predicted theoretically by Granger et al for the case of freely suspended single-walled nanotubes (SWNTs) [14, 15]. Unsupported SWNTs are expected to exhibit a remarkable type of ISs, referred to as ‘tubular’ ISs, having nonzero angular momentum and very long lifetimes (up to 0.1 ms [14]) when compared to ISs at metallic [16, 17] and graphite surfaces [18] (of the order of 10 fs). Zamkov et al predicted that the SWNTs should also reveal low- and zero-angular momentum ISs that have a reduced radius of localization (of the order of 1 nm) when compared to their ‘tubular’ counterpart (up to 10 nm and more) [19]. The first experimental evidence for the existence of low- and zero-angular momentum ISs at carbon nanotubes was provided for freestanding multi-walled nanotubes (MWNTs) by femtosecond time-resolved photoemission measurements [20]. Because of the variety of MWNT sizes in the investigated samples and the dependence of ISs on the tube diameter, the photoemission measurements result in a broadened IS spectrum that is a superposition of multiple image electron energies and cannot reveal the discrete nature of the ISs. Alternatively, local probing techniques, in particular scanning tunneling microscopy (STM) and spectroscopy (STS), should allow us to investigate IS phenomena of substrate-supported CNTs at the atomic scale.
with high-energy resolution. Recently, ISs of C\textsubscript{60} molecules supported by a nanostructured Ag/Pt(111) surface have been investigated using STM and STS by Ruffieux et al [12]. Via probing of the ISs the authors were able to map the surface potential landscape of the nanostructured substrate from which the site-specific adsorption of the C\textsubscript{60} molecules could be elucidated. Theoretical and experimental investigations of ISs at substrate-supported nanotubes are, however, still lacking, at least to the best of our knowledge.

Here, we demonstrate the existence of quantized ISs at double-walled carbon nanotubes (DWNTs) that are supported by atomically flat Au(111) surfaces. We relied on detailed STM imaging combined with STS measurements in the distance–voltage \( z(V) \) spectroscopy mode. In the latter spectroscopic mode the tunneling voltage \( V \) is ramped while the tunneling current \( I \) is kept constant (closed feedback loop) by increasing the distance \( z \) of the STM tip to the substrate as more and more (image-potential) states become available for tunneling [21]. Up to six DWNT ISs could be resolved within the investigated energy range and the ISs experience the typical Stark shift to higher energies with increasing electric field [21]. The energy at which the ISs occur appears to be very sensitive to local variations of the CNT surface, e.g. due to bending of the DWNT. Our findings hence illustrate that ISs at supported CNTs might be used as a sensitive probe to investigate local electronic interactions at the nanotube surface, e.g. near impurities and defects [22–25] as well as with the supporting substrate and between the outer carbon shells of double- and multi-walled nanotubes [26, 27].

STM and STS measurements are performed with a low-temperature STM set-up (Omicron Nanotechnology), operating at a base pressure in the \( 10^{-11} \) mbar range (\( T_{\text{sample}} \approx 4.5 \) K). Mechanically cut PtIr (10% Ir) tips are used, as well as electrochemically etched W tips that are cleaned \textit{in situ} as described in [4]. \( z(V) \) curves are recorded with a closed feedback loop with a grid size of \( 80 \times 80 \) up to \( 200 \times 200 \) points, from which \( dz/dV(V) \) curves are derived numerically. This way, \( dz/dV \) maps that directly reflect the local density of states (LDOS) [28] can be obtained at selected values of the tunneling voltage \( V \). The tunneling voltages indicated in the text and figure captions are with respect to the sample, while the STM tip is virtually grounded. Image processing was performed by Nanotec WSxM [29].

The nanotube material is produced by decomposition of methane on a Co/MgO catalyst in a temperature range from 1200 to 1300 K and is purified by hydrochloric acid treatment to remove the catalyst [30]. The purified carbon nanotube material (purity is around 98\%) is sonicated during 6 h at low power in 2-propanol and is deposited by drop-casting onto an Au(111) substrate [31]. Near to 100\% of the carbon nanotubes are DWNTs. We found that stable STM imaging of DWNTs on Au(111) could not be achieved at any settings of the tunneling current and voltage without \textit{in situ} annealing of the sample. Residual solvent contamination and contamination from exposure to ambient conditions may be present on the Au(111) surface on the as-prepared sample and consequently also in between the Au(111) surface and the DWNTs. Surface contamination may result in a bad electric contact between the DWNTs and the Au(111) surface and hence for the highly unstable STM imaging. Therefore, prior to STM investigation, the sample is annealed at moderate temperatures of around 700 K to remove this surface contamination. After annealing, the DWNTs can be imaged stably in a broad range of tunneling currents and voltages. This can be explained by (partial) evaporation of the surface contaminants during annealing, hence ensuring a good metallic contact between DWNTs and the Au(111) surface. After annealing DWNTs can be routinely retrieved within a scan area of about 1000 \( \times \) 1000 nm\(^2\) . The height (diameter) of the DWNTs on Au(111) is in the 1–4 nm range, which is typical for DWNTs [32], while the length is of the order of 1 \( \mu \)m, in agreement with atomic force microscopy observations.

In the inset in figure 1 (top) we present a typical topographic STM image of a DWNT, which crosses various flat Au(111) terraces that are separated from each other by monatomic steps. As can be seen upon closer inspection of the inset of figure 1 (top), the flat Au(111) terraces do not reveal the known herringbone reconstruction of the Au(111) surface that can typically be observed after repeated cycles of \textit{in situ} Ar ion sputtering and annealing at moderate temperatures [33].
Here, only in situ annealing can be applied to enhance the sample cleanliness, since Ar ion sputtering would destroy the DWNTs. The presence of surface contaminants during the annealing process may force the Au(111) surface to reconstruct, yielding a somewhat deformed Au(111) surface that does not show the typical herringbone reconstruction. The $z(V)$ spectrum in figure 1 (top) recorded at the DWNT reveals multiple steps at specific tunneling voltages due to the presence of quantized ISs. It can be seen that ISs are already formed at distances of the order of 1 nm away from the surface of the supported nanotube. These distances are similar to the radii of localization for low- and zero-angular momentum ISs formed at unsupported nanotubes [19, 20]. The ISs can be discerned more clearly in figure 1 (bottom), where we present the derivative $dz/dV(V)$ of the $z(V)$ spectrum in figure 1 (top). Vertical dotted lines connect the maxima in the $dz/dV(V)$ spectrum to the corresponding steps in the $z(V)$ spectrum. From a Lorentzian fit (red dotted line in the lower panel of figure 1) of the experimental data the full width at half-maximum (FWHM) of the IS maxima and hence the lifetime $\tau$ of the corresponding experimental ISs can be estimated. Using $\tau \approx h/\text{FWHM} = 658 \text{ meV}/\text{FWHM}$ [34], a lifetime in the 1–3 fs range is obtained. It must be noted, however, that the lifetimes extracted from $dz/dV(V)$ spectra obtained with a closed feedback loop underestimate the intrinsic lifetime of electron states. Pascual et al have shown that the varying tunneling barrier shape due to the varying electric field and tip–sample distance during the measurement, can cause broadening of the observed IS peaks up to a few times the intrinsic peak width [35]. In spite of the rather large uncertainty in our lifetime determination, we find that the lifetimes of ISs of supported DWNTs are about two orders of magnitude smaller than the lifetimes reported for tubular ISs at freestanding MWNTs as determined by photoemission measurements [20]. This large difference cannot be explained by the use of different measurement techniques only. Moreover, the enhanced lifetime of tubular ISs at unsupported nanotubes (up to 0.1 ms [14]) when compared to metallic surfaces (fs range [16, 17]) is theoretically predicted to be a general property for both single- and multi-walled carbon nanotubes [19]. Since the lifetimes derived here for supported DWNTs are of the same order of magnitude as those for metallic surfaces, our results are indicative of a significant coupling of the nanotubes to the underlying Au(111) substrate.

Next, we investigated the variation of the DWNT ISs along the cylindrical nanotube surface as well as the transition to the Au(111) ISs. In figure 2(a) we present a topographic STM image of another DWNT on Au(111). Figure 2(b) is a height profile taken along the blue arrow in (a). Two typical $dz/dV(V)$ spectra recorded at the correspondingly labeled locations in (a) are presented in figure 2(c). There appear to be clear differences in the energies at which the Au(111) and DWNT ISs occur. These differences may be linked to the different work functions of carbon nanotubes ($\approx 5.0 \text{ eV}$ [36]) and Au(111) ($\approx 5.55 \text{ eV}$ [37]), as well as to the cylindrical curvature of the DWNT surface. It was shown previously by Clinton et al that surface corrugation can significantly shift the energies at which ISs occur from the energies observed at flat surfaces [38]. Figure 2(d) is a 2D visualization of the $dz/dV(V)$ spectra taken along the blue arrow in (a). The transition between the Au(111) and DWNT ISs appears to be very ‘sharp’ rather than ‘smooth’ as observed for flat metallic islands on Au(111) surfaces [4]. Such a ‘sharp’ behavior is consistent with previous STS observations for C$_{60}$ molecules on Ag/Pt(111) [12]. Theoretical calculations similar to those of Zamkov et al [20], with the additional complication of the presence of the substrate and the electric field involved in STM measurements, will be required to achieve a quantitative description of our experimental results. Note that tip convolution effects need to be taken into account as well when considering the transition region between the Au(111) and DWNT ISs in theoretical calculations.

In addition, there appears a small ‘shoulder’ below the $n = 1$ DWNT IS maximum as well as a ‘bump’ around 5 eV in between the $n = 1$ and 2 ISs. Recently, a double Rydberg series of IP$_s$ was predicted by ab initio calculations [7], which has been confirmed by STS measurements for the case of mono- and bilayer graphene sheets grown on the surface of silicon carbide wafers [27]. The double series are most pronounced for monolayer graphene and, for graphite, evolve into a single series typical of metal surfaces [9, 21]. Considering the DWNT as a curved two-dimensional (2D) bilayer graphene surface, the features observed here may indicate the existence of a double Rydberg series of IP$_s$ at DWNTs, which can hence be expected to be more pronounced for SWNTs and to evolve into a single series for MWNTs.

In figures 3(c) and (d) we present the result of three $z(V)$ grid measurements for the DWNT shown in (a) (this tube is different from those shown in figures 1 and 2), recorded at various settings of the tunneling current, i.e. 0.1, 1.0 and 10.0 nA. This way, we were able to investigate the influence of the applied electric field between the STM tip and the DWNT on the DWNT ISs. It must be noted that upon further increasing of the tunneling current the DWNT under investigation was severely damaged and was cut into two pieces [39]. Figure 3(b) is a zoom-in image of (a) and reveals the atomic structure of the DWNT that is consistent with previous STM measurements for DWNTs [26]. The inset of figure 3(b) is a Fourier transform image of figure 3(b) and clearly reflects the hexagonal atomic arrangement of the DWNT. We note that all data in figure 3 are obtained with the same STM tip and that there did not occur any ‘tip change’ during the complete set of measurements presented in figure 3. It is well known that the energies at which the ISs occur strongly depend on the precise tip geometry [9], since the tip geometry determines directly the electric field and hence the resulting Stark shift experienced by the hydrogen-like ISs (described by equation 1) at the DWNT. Furthermore, as indicated above, both PtIr and W tips were used in our experiments. The different work function of both (tip) materials can be expected to influence the energies at which the ISs occur, since the tip work function determines (to a certain extent) the shape of the potential barrier experienced by the ISs. However, because of the strong dependence of the IS energies on the precise tip geometry, a systematic dependence of the IS energies on the tip material could not be
observed in our experiments. In figure 3(c) we present three 2D visualizations of the $d_z/dV(V)$ spectra (ranging from $V = 2.0$ to $10.0 \, \text{V}$) recorded along the blue arrow in figure 3(b) at the indicated values of the tunneling current. The energy of each of the ISs does not vary along the longitudinal direction of the DWNT for all settings of the tunneling current and even at locations where the DWNT is lying across a monatomic step at the Au(111) surface (not shown). On the other hand, figure 3(d) reveals a (nonlinear) shift of the DWNT ISs to higher energies with increasing values of the tunneling current, which is consistent with an enhanced Stark shift of the ISs due to the increasing electric field.

Finally, we investigated the influence of local variations of the DWNT surface structure on the DWNT ISs. In figure 4(a) we present an STM image of the end of a DWNT that exhibits a local bend by an angle around 45°. Figure 4(b) is a 2D visualization of $d_z/dV(V)$ spectra taken along the black arrow in (a). This kink was naturally observed and was not intentionally created by manipulation with the STM tip as was the case in [40]. While the IS energy does not vary across or along a straight and defect-free DWNT surface (figures 2(d) and 3(c)), it can be clearly seen in figure 4(b) that there occurs a change in IS energy when crossing the bent region of the DWNT surface, as if the nanotube consists of two different parts. The difference between these two regions is further illustrated in the $d_z/dV(V)$ maps presented in figures 4(c)–(e) that are recorded at the location indicated by the red dotted square in (a). The observed difference in these LDOS maps may indicate a different interaction between the two cylindrical graphene sheets of the DWNT for the two regions due to a shift of the relative positions that is caused by the bend and results in a modified surface potential experienced by the DWNT ISs. Alternatively, our observation may be related to the formation of a metal–semiconductor junction at the kink in the DWNT [22]. It was shown previously that kinked SWNTs (consisting of a metallic and a semiconducting part and fitted together by introducing pentagon–heptagon defect pairs [23, 24] in the kinked region) may result in the formation of a metal–semiconductor Schottky diode and exhibit a rectifying current–voltage behavior [22]. Note that the kink in figure 4(a) appears to be quite abrupt and no clear height increase is observed at the kink. Although we could not achieve atomic resolution with the STM tip used in this experiment, our observation may indicate that the kink is indeed related to the presence of atomic scale pentagon–heptagon defect pairs [23, 24]. We are convinced.
that our experimental results will spark further experimental and theoretical work related to ISs of supported carbon nanotubes.

In conclusion, we demonstrated the existence of ISs at the surface of supported DWNTs by relying on STS $z(V)$-grid measurements. The lifetime of the supported DWNTs is found to be about two orders of magnitude smaller than the lifetimes that have previously been obtained for ISs at unsupported MWNTs from time-resolved photoemission measurements [20]. The DWNT ISs exhibit a (nonlinear) Stark shift to higher energies with increasing electric field between the STM tip and the DWNT. The energy at which the ISs occur does not vary across the cylindrical DWNT surface, but is very sensitive to the presence of local surface defects that result, for example, from bending of the DWNT. ISs at supported nanotubes provide a novel playground for investigation of local electronic properties of nanotube surfaces.

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