Atomically Resolved Single-Walled Carbon Nanotube Intramolecular Junctions

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Published Version</td>
<td><a href="http://dx.doi.org/10.1126/science.291.5501.97">http://dx.doi.org/10.1126/science.291.5501.97</a></td>
</tr>
<tr>
<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:2757767">http://nrs.harvard.edu/urn-3:HUL.InstRepos:2757767</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dashboard.current.terms-of-use#LAA">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dashboard.current.terms-of-use#LAA</a></td>
</tr>
</tbody>
</table>
Intramolecular junctions in single-walled carbon nanotubes are potentially ideal structures for building robust, molecular-scale electronics but have only been studied theoretically at the atomic level. Scanning tunneling microscopy was used to determine the atomic structure and electronic properties of such junctions in single-walled nanotube samples. Metal-semiconductor junctions are found to exhibit an electronically sharp interface without localized junction states, whereas a more diffuse interface and low-energy states are found in metal-metal junctions. Tight-binding calculations for models based on observed atomic structures show good agreement with spectroscopy and provide insight into the topological defects forming intramolecular junctions. These studies have important implications for applications of present materials and provide a means for assessing efforts designed to tailor intramolecular junctions for nanoelectronics.
(n,m) indices define the nanotube structure through the vector \( \mathbf{C}_n = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the unit vectors of the graphene hexagonal lattice. For the semiconducting and metallic portions, these indices are (21,–2) and (22,–5), respectively. SWNT segments with these indices can be joined seamlessly along a common axis using different configurations of 5–7 defects. Two low-energy structural models are shown (Figure 2A), which have been optimized using molecular mechanics energy minimization. Model I consists of three separated 5–7 pairs and Model II has two isolated 5–7 pairs and one 5–7/7–5 pair. It is possible to evaluate the viability of these atomic models by calculating the local electronic density of states (LDOS) and comparing these with experiment. The results from our tight-binding calculations (15, 25) (Figure 2B) show that LDOS for Model I matches the experimental data well. Specifically, the first VHS of the semiconducting segment decays across the IMJ into the metallic segment with a decay constant similar to that in the experiment. In contrast, the LDOS calculated for Model II exhibits low-energy states around –0.10 eV, which are not observed in our experimental data. Hence, we believe that Model I can be reasonably assigned to the structure for the observed IMJ. Our new results and previous calculations (5–8) show that the absence or presence of localized states at the M-S junction reflect the specific configuration of 5–7 defects. Because this could be used to vary device properties, it will be interesting to see whether these configurations can be controlled in the future.

We also characterized a M-M IMJ junction using similar methods (Figure 3). The atomically resolved image (Figure 3A) suggests a large difference in diameters but similar chiral angles for the upper and lower segments of IMJ structure, \( d = 1.23 \pm 0.05 \text{ nm} \) and \( \theta = 24.3^\circ \pm 0.6^\circ \), \( d = 1.06 \pm 0.05 \text{ nm} \) and \( \theta = 23.8^\circ \pm 0.6^\circ \), respectively. The local spectroscopy data recorded away from the IMJ region (Figure 3B) demonstrates that the magnitude of the first VHS gap for the lower segment is larger than that recorded on the upper segment. Thus, these gaps are consistent with the diameters determined from the images. Moreover, they show that both segments are metallic SWNTs. In addition, spatially resolved spectroscopy data recorded...
across the IMJ (Figure 3C) shows new features not observed in the M-S IMJ discussed above; that is, there are low-energy peaks at –0.55 and –0.27 eV not present in the spectroscopy data recorded away from the junction. These peaks appear to decay slowly from the IMJ into the bulk of the larger diameter segment but quickly into the smaller segment.

We determined the \((n,m)\) indices of the larger and smaller segments of the IMJ structure using the iterative method above and find the best fits to be for values of \((11,8)\) and \((9,6)\), respectively, which are both metallic tubes. To check the consistency of this assignment, tight-binding calculations (25) were used to evaluate the LDOS for isolated \((11,8)\) and \((9,6)\) tubes. Comparison of the calculated and experimental LDOS (Figure 3B) shows excellent agreement and substantiates our assignment of the indices and the M-M character of the junction. The \((11,8)\) and \((9,6)\) SWNT segments can be joined seamlessly along a common axis using different configurations of 5–7 defects. A specific model (Figure 4A) we analyzed consists of two separated 5–7/7–5 pairs. It is also possible to connect the \((11,8)\) and \((9,6)\) segments using two or three 5–7 pairs, although our calculations suggest that these are less likely (26). The LDOS obtained from our \(\pi\)-only tight-binding calculation (Figure 4B) shows reasonable agreement with the experimental observation. Specifically, the low-energy peak at –0.55 eV matches that observed in experiment; however, we do not detect the other peak at –0.27 eV in our \(\pi\)-only calculations. We also evaluated and compared the decay of this peak in both directions from the IMJ and found that the calculated (1.6 nm\(^{-1}\)) and experimental (1.9 nm\(^{-1}\)) decay into the \((9,6)\) segment agree better than calculated (2.6 nm\(^{-1}\)) and experimental (4.9 nm\(^{-1}\)) decay into the \((11,8)\) segment.

We believe that the proposed atomic model represents a reasonable description of the IMJ but also realize that our calculations have limitations. In particular, the greater structural distortions required to join the \((11,8)\) and \((9,6)\) tubes probably require inclusion of at least \(2\sigma\) and \(2\pi\) orbitals to describe properly the electronic structure. More detailed calculations should help to understand the origin of all of the localized states detected experimentally as well as the interesting asymmetry in the decay of these states from the IMJ interface.

The direct atomically resolved characterization of IMJs in as-grown SWNT materials by STM has important implications and opens exciting opportunities on several fronts. We have demonstrated unambiguously that IMJs are present in SWNT samples, and statistics show that topological defects occur with a relatively high frequency in these samples grown by laser ablation, in contrast to previous expectations. The common occurrence of these defects could have important implications for the interpretation of electrical transport and mechanical measurements. These studies provide experimentally derived atomic-level junction models that will enable an important dialog between experiments and further high-level calculations designed to reveal details of IMJ physics. We also believe that STM characterization of IMJs can provide critical information and a feedback

---

**Figure 3.** Structure and spectroscopy of a M-M IMJ. (A) Constant-current image of \((11,8)/(9,6)\) junction recorded at \(V_x = 500\) mV and \(i = 150\) pA. The white arrow highlights the junction interface. Bar, 1 nm. Symbols are as in Figure 1. (A) and (C). The image of the upper SWNT segment is more complex than that found in typical data. Although detailed analysis is beyond the scope of this paper, recent calculations suggest that the observed structure in the image may be due to conduction electron scattering (22). (B) \(dI/dV\), recorded at the upper (Δ) and lower (*) locations indicated in (A). The corresponding calculated DOS for \((11,8)\) and \((9,6)\) SWNTs are shown above and below the experimental curves, respectively. (C) Spatially resolved \(dI/dV\) recorded across junction at the positions indicated in (A). New peaks at –0.55 and –0.27 eV in the junction region are highlighted by solid black and open arrows, respectively.

**Figure 4.** Atomic model and electronic properties of the M-M IMJ. (A) Model of the \((11,8)/(9,6)\) junction containing two separated 5–7/7–5 pairs, which are highlighted with solid red and blue spheres. The view presented was obtained by rotating about the axis until the observed structure was similar to the experimental image (Figure 3A). (B) Calculated LDOS curves corresponding to the six positions indicated in (A). The solid black and open arrows correspond to the same positions highlighted in Figure 3C. (C) Spatial decay of the localized junction state at –0.55 eV. The solid and dashed lines correspond to fits to the experimental and calculated data, respectively. The origin, negative position \((11,8)\) side, and positive position \((9,6)\) side are indicated in (A). The decay constants \(k_x\) were obtained by fitting to \(\exp[-k_x x]\).
mechanism for growth studies designed to establish rational pathways for controllably producing IMJs in the future.

References & Notes

16. For example, a recent STM study suggests that the bend in a SWNT tube is an IMJ [L. C. Venema, et al., Phys. Rev. B 62, 5238 (2000)]. However, the absence of atomic resolution makes it impossible to distinguish whether the observed “kink” connects two different tubes rather than corresponding to a simple bend. In addition, the VHS peaks above and below the bend are not consistent with the SWNT diameters. Hence, it is possible that the observed spectroscopic features are due to effects of bending (15).
26. Preliminary tight-binding calculations for these two models do not exhibit good agreement with experiment (18).
27. We thank M. S. Gudiksen, T. W. Odom, H. Park, and P. Kim for helpful discussion. Supported by the NSF.