

Covalent Bond Formation to a Carbon Nanotube Metal

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The pseudo-one-dimensional (pseudo-1D) conjugated electronic structure of single-walled carbon nanotubes (SWNTs) allows them to exhibit semiconducting and metallic properties and to exhibit ballistic transport (*I*). We show that their unique electronic structure also offers the opportunity for new horizons in chemistry by exploring the response of the Fermi level (E_F) electronic structure of the metallic SWNTs to carbon-carbon bond formation at the nanotube surface.

Ionic chemistry (doping) with electron acceptors introduces holes into the valence band of the nanotubes that can lead to the removal of the interband transition between the first set of singularities in the density of states (DOS) of the semiconducting SWNTs (2). However, the most prominent modification to the spectra of the hole-doped SWNTs occurs in the far-infrared (FIR), where there is a very strong increase in the intensity of excitations near E_F due to intraband transitions (3). Although ionic chemistry does not change the band structure, it does create partially filled metallic bands, and the local electrostatic fields, due to the counterions, are too weak to cause localization.

Covalent chemistry simultaneously weakens the strength of all of the interband transitions in both the semiconducting and metallic SWNTs (2, 4) because the saturated bonds function as defects. This perturbs the periodicity of the pseudo-1D lattice and eventually destroys the electronic band structure altogether (unlike ionic chemistry, where the electronic transitions disappear sequentially in order of increasing energy).

However, the largest effects of covalent chemistry should occur in the metallic SWNTs because the metallic state should be extremely sensitive to the occurrence of defects introduced by saturation of the delocalized electronic struc-

ture. In particular, these effects should be most strongly manifested in the transitions at E_F because it is these transitions that are characteristic of a metal, that is, a species without a gap in the energy band spectrum. In fact, we are not aware of any intrinsic carbon-based metals except for the SWNTs, and therefore they provide a unique opportunity to probe the effects of carbon-carbon bond formation on the Fermi level electronic structure of a true metal. (Graphite, for example, is a semimetal, whereas a single graphene sheet and turbostratic graphite are zero-gap semiconductors.)

For our experiments, we chose SWNTs made under HiPco (high-pressure CO) conditions that were rendered soluble in organic solvents by functionalization with octadecylamine (ODA) (2). Reaction of dichlorocarbene generated from $\text{PhHgCCl}_2\text{Br}$ (5) forms carbon-carbon bonds to the body of the SWNTs (2). This type of wall chemistry introduces cyclopropane functionalities in place of the partial double bonds initially present in the SWNT-conjugated electronic structure, and each addition saturates a conjugated bond, thereby converting the valence of a pair of carbon atoms from sp^2 to sp^3 (Fig. 1A). We carried out reactions on soluble SWNTs (s-SWNTs) with a range of stoichiometries to introduce different degrees of

saturation into the SWNTs, and we analyzed the resulting products by energy-dispersive x-ray spectroscopy.

The samples were redispersed in tetrahydrofuran or dimethylformamide and cast as semitransparent films on either sapphire or silicon substrates, in order to obtain spectra from the FIR to the ultraviolet. The results are summarized in Fig. 1B, where it may be seen

that the pristine s-SWNTs exhibit the very strong FIR absorption characteristic of a metal, together with the other interband electronic transitions of HiPco SWNTs (4). The strong FIR absorption of the soluble metallic SWNTs shows that the dissolution procedure does not damage the conjugated electronic structure of the SWNTs and matches previous spectra of unfunctionalized SWNTs (3, 6). Upon reaction with dichlorocarbene, however, oscillator strength is rapidly lost from the FIR band, showing the sensitivity of the metallic properties to the introduction of defects (7, 8). Saturation of 12% of the partial double bonds reduces the intensity by about 50%, whereas saturation of 23% of the conjugated electronic structure removes over 90% of the intensity. The intensity in the FIR is transferred to the visible region and, though there are no new features, the changes suggest a series of new excitations in the 0.25 to 3 eV range. This result is consistent with the picture of smaller condensed aromatic systems evolving from the SWNTs that initially possess translational symmetry and well-developed band electronic structure.

Covalent chemistry on the sidewall of a metallic SWNT rapidly opens a gap at E_F , changing a metal to a semiconductor. Thus, there is a clear differentiation from ionic chemistry, which strongly increases the intensity of the FIR absorptions by doping of the semiconducting SWNTs to produce enhanced metal-like intraband transitions. The results provide a clear signature for SWNTs chemistry and show that chemical effects, like many other physical processes, are dominated by the electronic structure at E_F .

References and Notes

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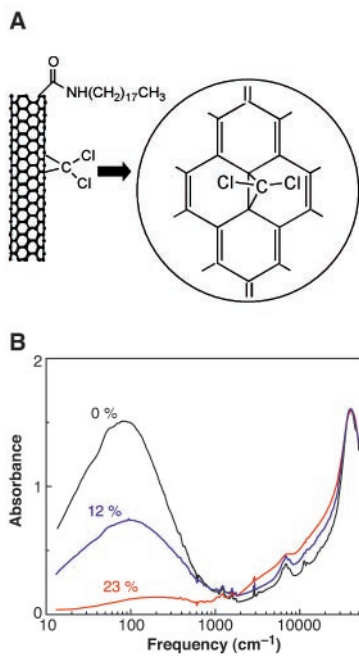


Fig. 1. (A) Schematic representation of the binding of dichlorocarbene to SWNT. (B) Absorption spectra of films of soluble SWNTs functionalized with dichlorocarbene. The curves are labeled with the degree of functionality. Spectra are normalized to the value of the absorption at the π -plasmon peak at $37,000\text{ cm}^{-1}$.