

Engineering the electronic structure and transport properties of carbon nanotubes via sidewall chemical functionalizations: a first-principles approach

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We have combined large-scale, Γ -point electronic-structure calculations with the maximally-localized Wannier functions approach to calculate efficiently and inexpensively the band structure and the quantum conductance of complex systems containing thousands of atoms. The method relies on our ability to describe the Hamiltonian matrix in real-space with a minimal but also almost complete basis set of maximally-localized Wannier functions. Very large systems can be dealt with by the seamless combination of sub-units' Hamiltonians, with small and in principle linear-scaling computational costs while maintaining full ab-initio accuracy thanks to the transferability of the localized orbitals. This approach allows us to characterize the effects of covalent functionalizations on the electronic transport properties of carbon nanotubes tens of nanometers long. Binding of aryl moieties or even atomic hydrogen to sidewall carbons induces sp^2 to sp^3 rehybridization, rapidly destroying the original π -electron manifold of the pristine metallic tubes. The band structure and transport properties are found to be much less dependent on the chemical nature of the electropositive or electronegative residues of the organic ligands, than on the pattern and topology of the sp^3 rehybridizations. On the other hand, cycloaddition of nitrenes or carbenes is able to recover the sp^2 character of the sidewall carbons, whenever they induce the cleaving of the bond between backbone atoms. Much weaker perturbation and scattering from the ligand thus ensues, allowing to preserve and even control the unique electronic properties of the metallic graphitic manifold.