

## CHARACTERISATION OF DIFFERENT FUNCTIONALISATION PATTERNS ON SINGLE-WALLED CARBON NANOTUBES BY SCANNING TUNNELING MICROSCOPY

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Single-Walled Carbon Nanotubes (SWCNT) are seamless cylinders of a few nanometers diameter and microns in length. They can be either metallic or semiconducting, depending on their diameter and the spiral alignment of the hexagonal rings of graphite along the tube axis. Numerous schemes have been proposed to functionalise SWCNT in order to change and control their properties. However, a fundamental understanding of the structure and properties of the functionalised SWCNTs on the atomic level is still lacking.

We report the discovery of long-range (several nanometer) induced reactivity leading to highly regular, long-distance patterns using scanning tunneling microscopy. Our observations hold both for SWCNT's functionalised by the Bingel reaction [1, 2] and by nucleophilic bipolar 1,3-cycloaddition. The observed distances are far beyond what one would expect from steric hindrance alone. Figure 1 is an image of several SWCNT's exhibiting a peculiar pattern after functionalisation by the Bingel reaction. The functional groups are spaced at about 4.6 nm (i.e. approx. 20 carbon rings) along a number of tubes. Figure 2 was obtained from a different sample on a different instrument. In this particular case, a separation of about 2.3 nm is observed. A number of other distances have also been observed. Similar patterns have been found after the 1,3-cycloaddition of the pyrrolidine moiety onto nanotubes.

We postulate that long range fluctuations in the electron density along the sidewall (due to pre-existing defects or reacted sites) are at the origin of the observed patterns. It is worth noting that both systems under study involve a nucleophilic attack on the carbon nanotube sidewall. The reaction mechanism for the Bingel reaction [2] has been postulated to be a nucleophilic addition of the deprotonated species of diethyl bromomalonate followed by an intramolecular substitution of the halogen in a [2+1] cycloaddition. A nucleophile will be more likely to attack the SWCNT at sites with a reduced electron density, leading to the site selectivity of subsequent attachments. The large distance between the functional groups in the patterns (e.g. 4.6 nm vs. 0.14 nm for a C=C bond) cannot be explained by steric effects or simple chemical bonding arguments. The attachment of the first group to the nanotubes alters the electronic structure, inducing reactive sites in a regular pattern. The process of induced reactivity is illustrated in Figure 3. The varying distances between groups between different tubes is likely due to the varying diameter and helicity of the nanotubes, leading to a different electronic structure and hence a different periodicity of electron-deficient locals.

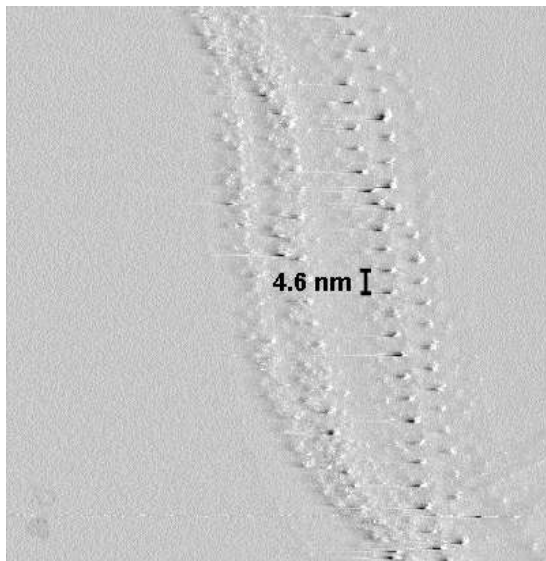
We are working to expand our findings to other conditions and reaction types. Our findings have far-reaching implications for the development of selective synthetic methods for functionalised SWCNTs with specific properties.

**Reference:**

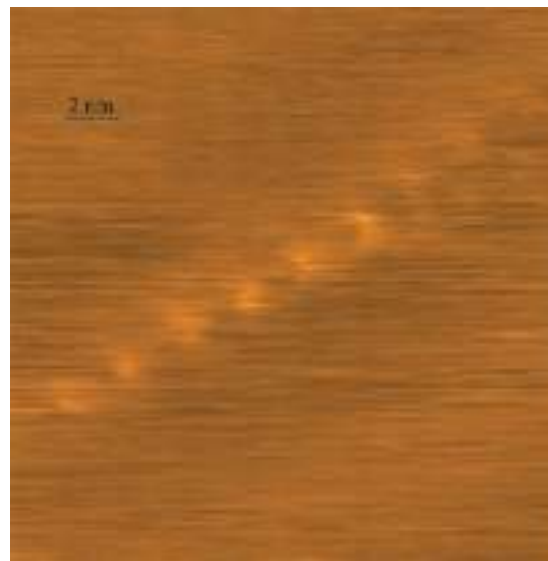
[1] K. A. Worsley, K. R. Moonosawmy, and P. Kruse, Periodicity in Carbon Nanotube Sidewall Functionalisation due to Long-Range Induced Reactivity.( in preparation, to be submitted to Nanoletters)

[2] Bingel, C., Cyclopropanierung von Fullerenen. *Chemische Berichte* 1993, 126, 1957-1959.

**Figures:**



**Figure 1**



**Figure 2**



**Figure 3:** Schematics illustrating the process of induced reactivity by the nucleophile.