Influence of functionalization with perfluoropolyether peroxide on surface and conductive properties of multi-walled carbon nanotubes

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Multi-Walled Carbon Nanotubes (MWCNTs)

Carbon Purity

90%

Synthesis

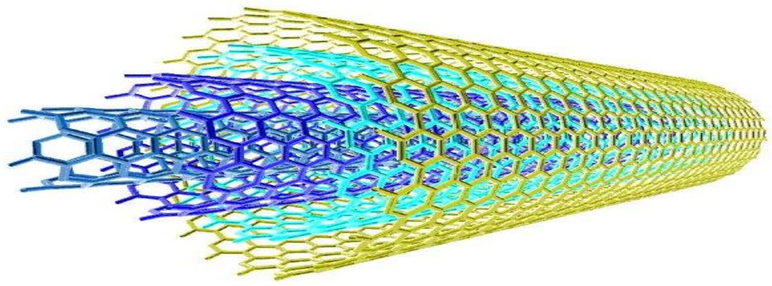
(CVD)

Average Diameter

9.5 nm

Average Length

1.5µ



Multi-Walled Carbon Nanotubes (MWCNTs)

Carbon Purity

95%

Synthesis

(CVD)

Average Diameter

13-16 nm

Average Length

1->10 µ

The linear PFPE peroxide **(Fomblin® Z PFPE peroxide)** was prepared industrially through the oxidative photopolymerization of tetrafluoroethylene (TFE).

$$CF_2{=}CF_2 + O_2 \xrightarrow[T< -60\ ^0C]{\text{UV light; Solvent}} T\text{-}O(CF_2CF_2O)_m(CF_2O)_n(CF_2CF_2OO)_p(CF_2OO)_q\text{-}T'$$

$T, T' = CF_3, C(O)F, CF_2C(O)F$

Z-Fomblin® Peroxide

Average Molecular Weight

~29000 u

C_2/C_1

1.15

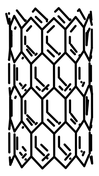
Peroxidic Oxygen

1.3% $_{wt}$

Equivalent weight

~1200 u

PFPE Radical Addition Reaction

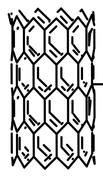


Perfluoropolyether Peroxide (PFPE Peroxide)

$$+\ T\text{-}O(CF_2CF_2O)_m(CF_2O)_n(O)_vT' \longrightarrow$$

AMW 29000; m/n 1.15; v ~24

$T, T' = CF_3, C(O)F, CF_2C(O)F$



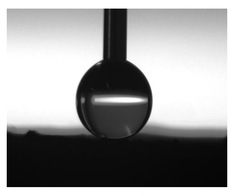
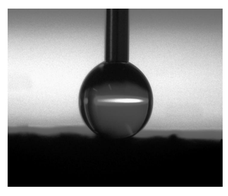
Linked Perfluoropolyether (Linked PFPE)

$$CF_2O[(CF_2CF_2O)_m(CF_2O)_n]T + v\ CF_2O$$

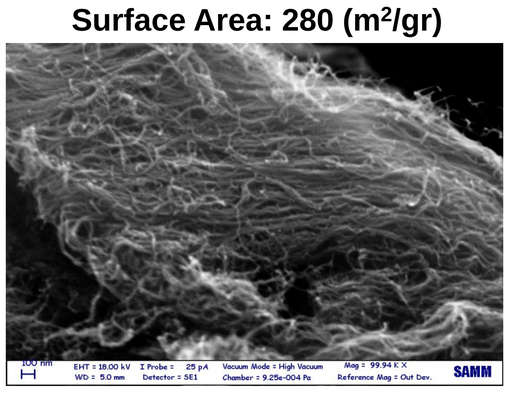
The thermal-induced homolysis of peroxidic bonds in linear PFPE peroxide generates reactive radical species with a PFPE structure, which are able to form covalent bonds on the sidewall of the MWCNTs.

S. Talaeemashhadi, M. Sansotera, W. Navarrini, et al. *Carbon*. **59**, 150-159 (2013).

The CA measurement on molded pellets of untreated MWCNTs revealed that the water droplets were adsorbed in few second (2-4 s) by the carbonaceous matrix.
The covalent linkage of PFPE chains conferred superhydrophobic properties to the MWCNTs surface and on molded pellets of PFPE-modified MWCNTs CA values around 165 were measured. The XPS data showed that the fluorine content on the MWCNTs surface appeared after chemical treatments with linear PFPE peroxide.

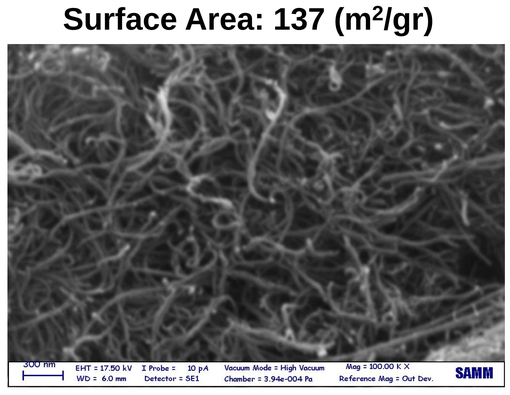
	MWCNTs (purity 90%) treated with 100%$_{wt}$ Z Peroxide	MWCNTs (purity 95%) treated with 100%$_{wt}$ Z Peroxide
%F_{at}–XPS	6.5%	5.4%
		
Static C.A. (°)	168 °	163 °
C.A. Hysteresis (°)	4.5 °	4.7 °

Surface Area: 280 (m^2/gr)



F(%$_{at}$) 6.5%

Surface Area: 137 (m^2/gr)

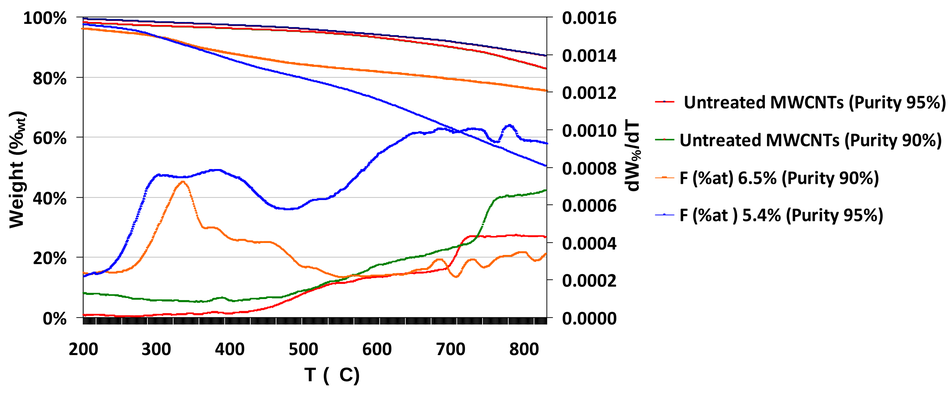


F(%$_{at}$) 5.4%

The untreated MWCNTs with 90 and 95% purity have surface area of 389 and 214 m^2/g, respectively.
The treatment with linear PFPE peroxide covered the surface of carbon nanotubes with PFPE chains which reduced the surface area of MWCNTs.
The SEM images revealed that the MWCNTs have maintained their bundled aggregation and no disaggregation occurred.

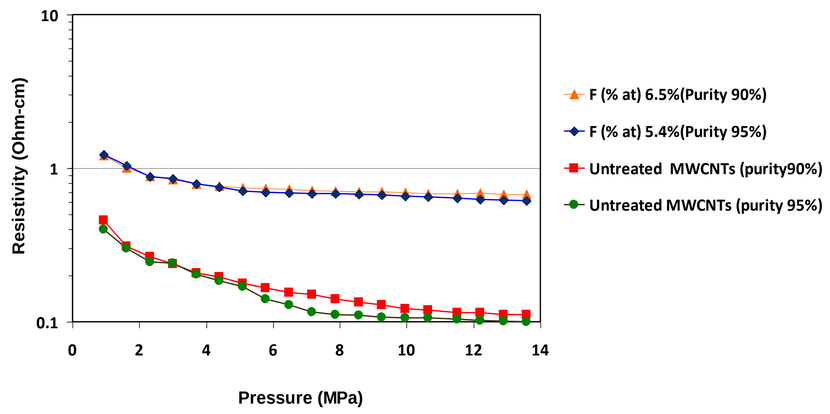
M. Sansotera, S. Talaeemashhadi, W. Navarrini et al. submitted to *JMR*.

Thermal Stability



The TGA measurement revealed that the degradation of untreated MW-CNTs started around 450 C. The samples treated with linear PFPE peroxide showed a weight loss in two separated steps: the first weight loss was approximately between 240-450 C and it was due to the degradation of PFPE chains on the sidewall of MWCNTs; a second weight loss started after 450 C and it can be ascribed to the degradation of modified parts of carbon nanotubes.

Electrical Resistivity



The conductivity measurements evidenced that the conductive properties of the MWCNTs treated with PFPE peroxide were maintained, even if the surface properties significantly changed. These results suggest that the functionalization of MWCNTs with linear PFPE peroxide occurs mainly at the outer tube while the inner tube remains almost unaltered.

Conclusion

- **The covalent linkage of PFPE chains on MWCNTs surface was obtained by means of thermal decomposition of the peroxidic moieties of linear PFPE peroxide.**
- **The linkage of PFPE chains conferred superhydrophobic properties to the MWCNTs surface.**
- **The covalent linkage of PFPE chains weakly influenced on thermal stability of MWCNTs.**
- **The resistivity measurements showed that the conductive properties of PFPE treated MWCNTs were maintained.**

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