Functionalization of Nanodiamonds with Perfluoropolyether Peroxide Via a Facile Thermochemical Process

Davide Ceriotti[1]*, Piergiorgio Marziani[1], Luca Magagnin[1,2], Elodie Petit[3], Samar Hajjar-Garreau[4], Julien Parmentier[4], Marc Dubois[3]†, Maurizio Sansotera[1,2]†.

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Synthesis procedure

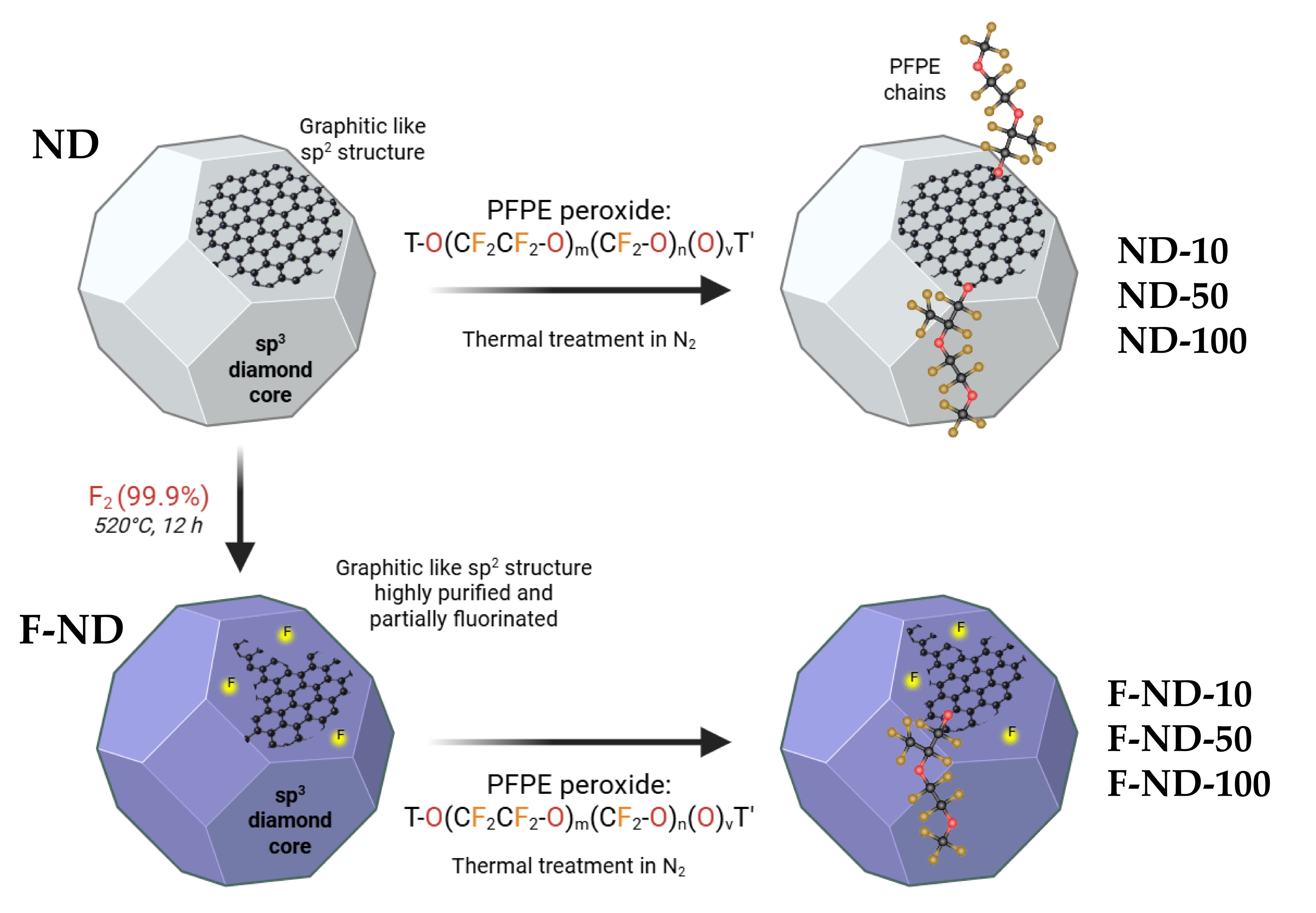
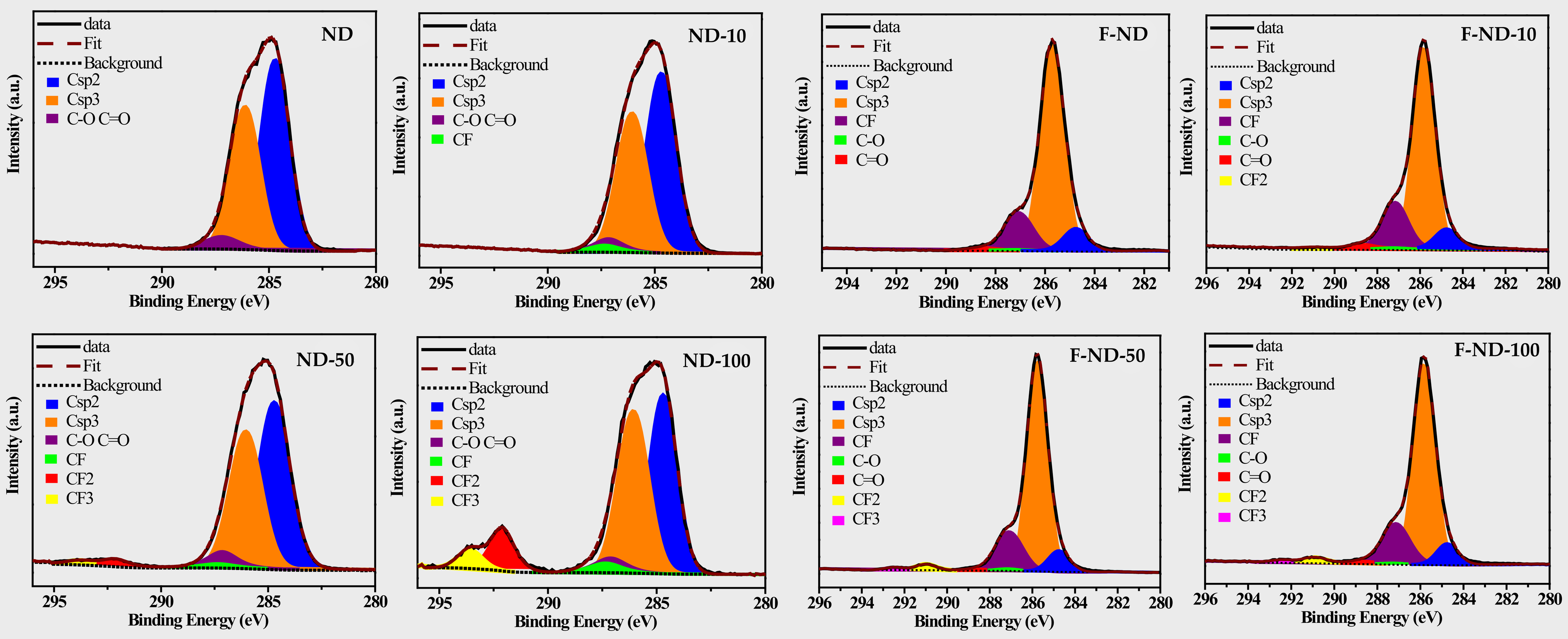


Fig 1. Synthesis of F-ND and functionalization with PFPE of F-NDs and NDs.

Nanodiamonds characterization

Functionalized nanodiamonds (NDs) and fluorinated nanodiamonds (F-NDs) were characterized by FTIR-ATR spectroscopy and solid-state NMR to identify the functional groups present on the surface, by XPS and TGA to quantify the fluorine and the bound PFPE, and finally by contact angle to measure the increase in hydrophobicity.



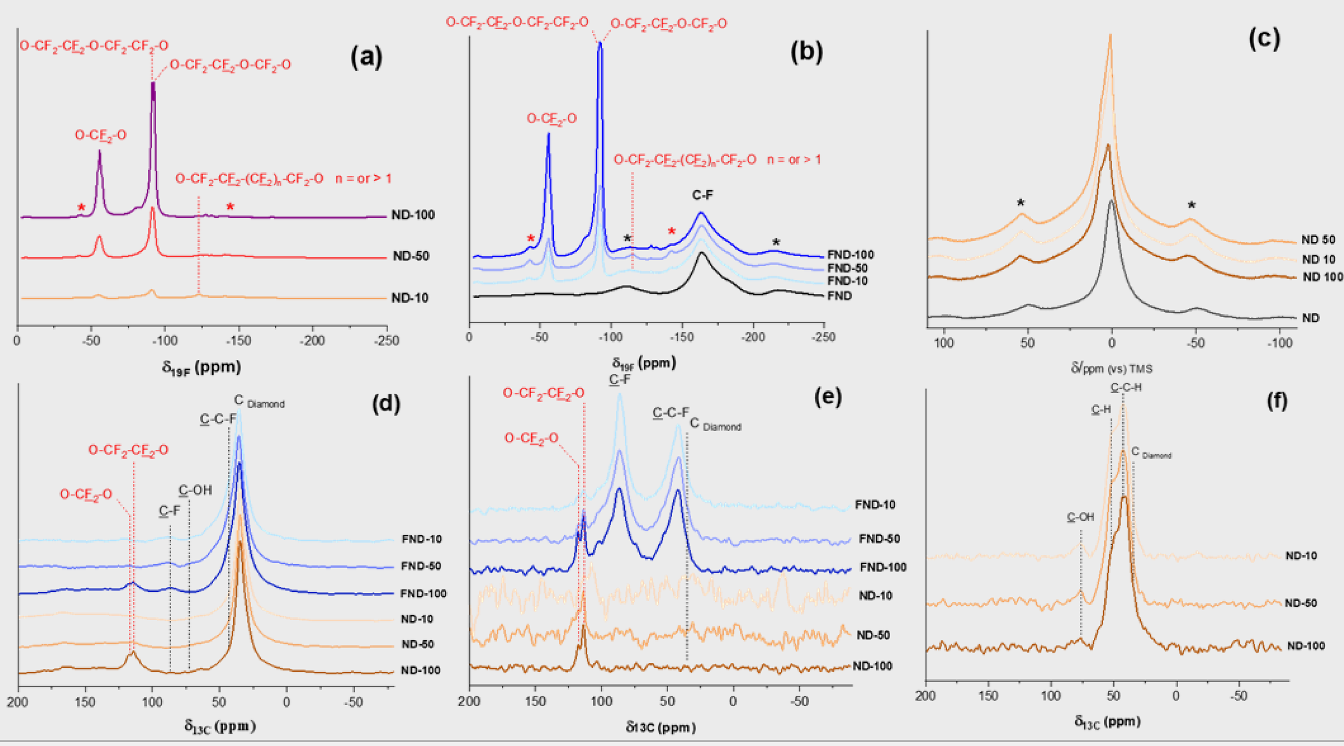


Fig 2. High resolution XPS spectra at C 1s region of the ND, ND-10, ND-50 and ND-100 sample (*top left*), F-ND, F-ND-10, F-ND-50 and F-ND-100 sample (*top right*).

Solid state MAS NMR spectra ^{19}F (14 kHz) (a) and (b); ^{1}H (14 kHz) (c), ^{13}C (d), $^{19}F \rightarrow {}^{13}C$ CP (10 kHz) (e) and $^{1}H \rightarrow {}^{13}C$ CP (10 kHz) (f) (*Bottom left*).

TGA quantification

Pristine NDs showed an average higher degree of PFPE functionalization compared to the fluorinated ones. The presence of C–F bonds in F-NDs decreased the number of C sp² available for the perfluoroalkyl reaction in PFPE functionalization.

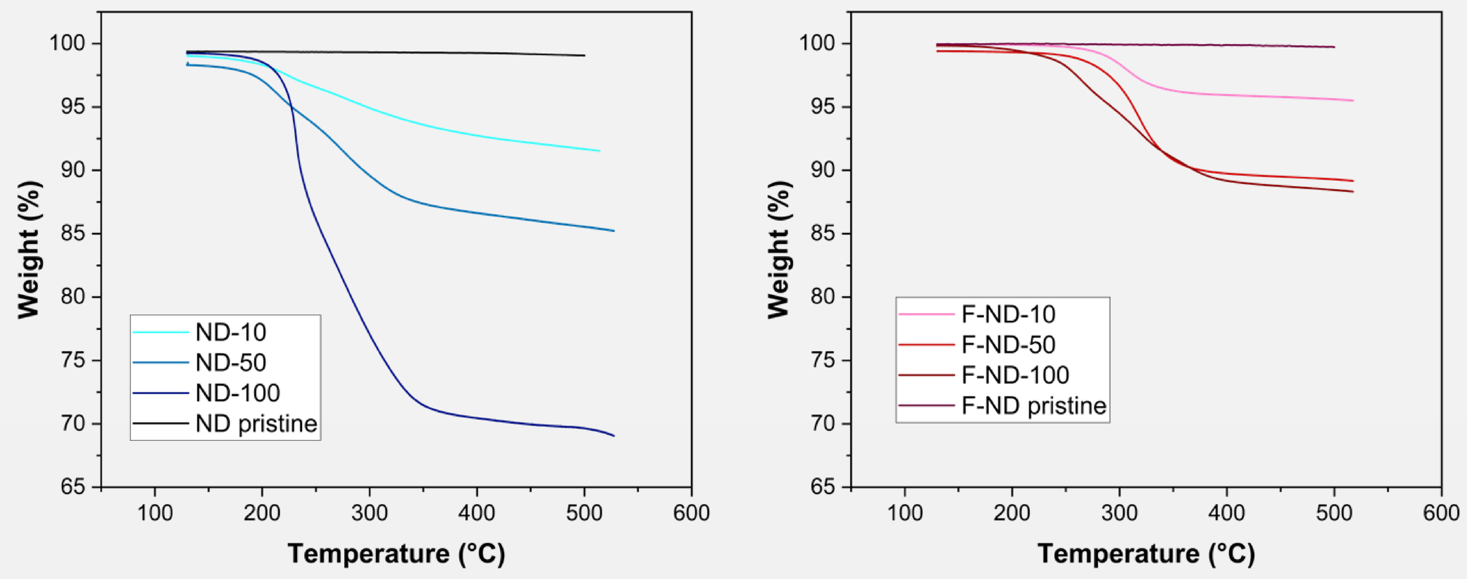


Fig 3. TGA analysis of PFPE-functionalized NDs (blue) and F-NDs (red).

Water contact angle

The sample F-ND-100 exceeded the **super-hydrophobicity** threshold by showing a water contact angle higher than 150°.

Sample	PFPE/ND Ratio	WCA (°)
ND	-	n.m
ND-10	1:10	n.m
ND-50	1:2	90°
ND-100	1:1	132°
F-ND	-	118°
F-ND-10	1:10	142°
F-ND-50	1:2	145°
F-ND-100	1:1	**153°**

Tab 1. *Water contact angle data with static droplets on nanodiamond samples functionalized with different amounts of PFPE peroxide.*

Dispersion properties

The dispersibility of functionalized NDs in solvents was investigated in chloroform and in a fluorinated solvent (Galden® HT110). In chloroform, pristine and functionalized nanodiamonds have precipitated at the bottom of the vial after 1h. In HT110 **they remained progressively more dispersed** as the functionalization degree increased.

Sample	Dispersibility (mg/mL) ±0.05
ND	-
ND-10	<0.1
ND-50	0.34
ND-100	0.93
F-ND	0.38
F-ND-10	0.31
F-ND-50	0.54
F-ND-100	0.77

Tab 2. *Dispersion, after 1 h, of pristine and functionalized NDs and F-NDs in Galden® HT110.*

Conclusions

PFPE-functionalization was successfully performed on NDs and F-NDs and the wettability and the dispersibility of the starting materials were modified conferring hydrophobicity to the surface and improving the interactions with low interface free energy media. Before the treatment, bare NDs were characterized by the presence of oxygenated groups on their surface resulting in an overall hydrophilic behavior; in F-NDs oxygenated groups were converted in C–F bonds conferring a marked hydrophobic character to the surface. PFPE-functionalization increased the hydrophobicity on both NDs and F-NDs reaching super-hydrophobicity. Such properties make these materials promising for use as additives in lubricating oils and composites, as well as for wear resistance, advanced electronics and biomedical applications.

*Presenting author: **Davide Ceriotti**, davide.ceriotti@polimi.it

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1. Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy.
2. Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (UdR-PoliMi), via G. Giusti 9, 50121 Firenze, Italy.
3. Université Clermont Auvergne, CNRS, ICCF 24, avenue Blaise Pascal 63179 Aubière, France.
4. Institut de Science des Matériaux de Mulhouse - IS2M - UMR 7361, Université de Haute-Alsace, 15 rue Jean Starcky, 68057 Mulhouse, France.

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