Nikolaev Institute of Inorganic Chemistry
Siberian Branch of Russian Academy of Sciences

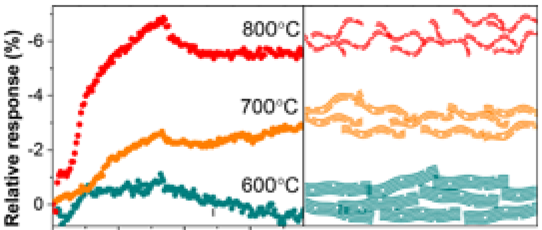
X-RAY PHOTOELECTRON SPECTROSCOPY AND NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY STUDY OF SYNCHROTRON RADIATION EFFECTS ON FLUORINATED GRAPHITE INTERCALATED NITROGEN TETROXIDE

G.I. Semushkina, L.G. Bulusheva, G.N. Chekhova, A.V. Okotrub, D.V. Pinakov, I.P. Prosvirin, Yu.V. Fedoseeva

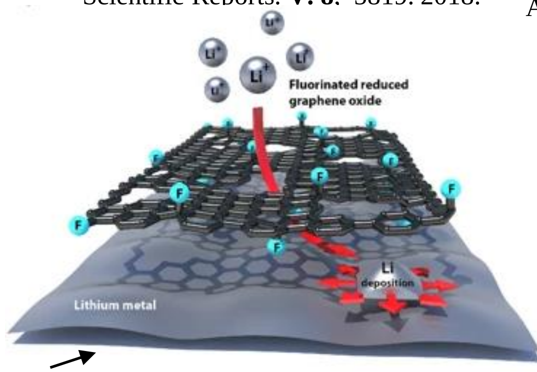
Synchrotron and Free electron laser Radiation: generation and application (SFR-2020)

Scientific relevance

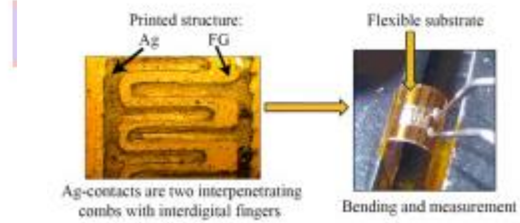
Sysoev V.I., Guselnikov A.V., Katkov M.V. and etc. // J. Nanophotonics. – 2016, V. 10 – P. 012512.



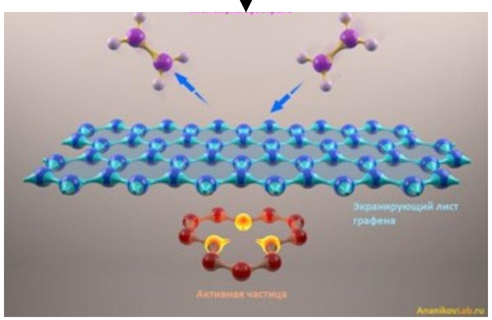
Jerney Bobnar, Matic Lozinsek, Gregor Kapun // Scientific Reports. **V. 8**, 5819. 2018.



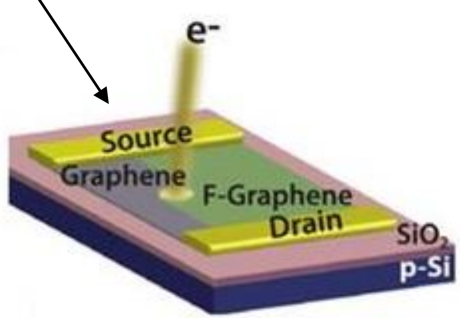
Author links open overlay panel I.V.Antonova, I.I. Kurkina, A.K. Gutakovskii and etc. // Materials Design. V.164. 2019, 107526



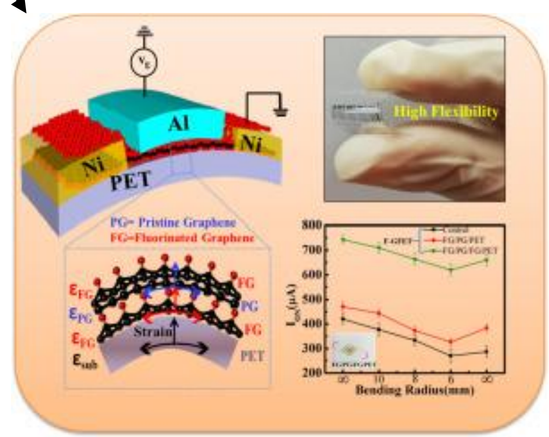
2016 **2018** **2019** **2020**



A. E. Sedykh, E. G. Gordeev, E. O. Pentsak and V. P. Ananikov // Phys. Chem. Chem. Phys. 2016, 18, 4608.

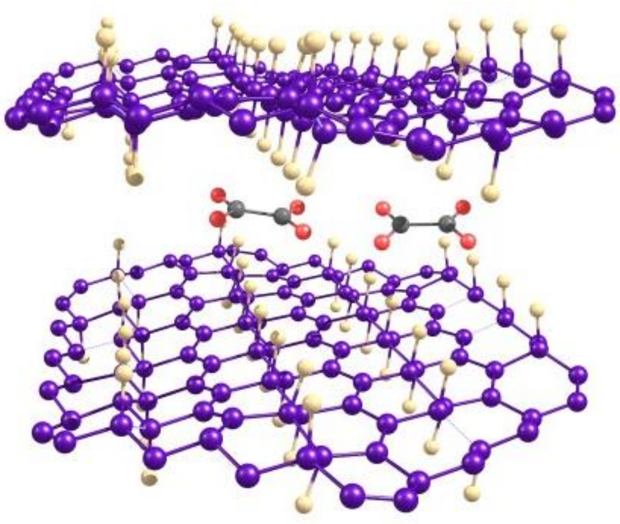


A De Sanctis, S Russo, M F Craciun, A Alexeev and etc. // *in* Interface focus: a theme supplement of Journal of the Royal Society interface. 2018



Mamina Sahoo, Jer-Chyi Wang, Yuta Nishin // Applied Surface Science. 2020.V.499, 143839

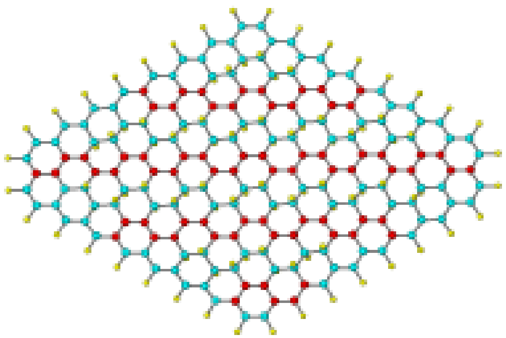
The object of study



1) $16C + Br_2 \rightarrow 2C_8Br.$

2) $BrF_3 + Br_2 \Leftrightarrow 3BrF$

$6C8Br + 8(2BrF_3 + Br_2) \rightarrow 24(C2F \cdot ⅓BrF_3) + 15Br_2.$



armchair chains

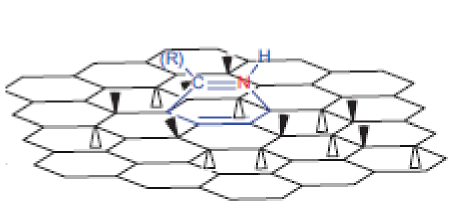
L.G. Bulusheva, A.V.Okotrub, N.F. Yudanov Physi. Low-Dim. Struct. 7/8 (2002) pp.1-14
A.Vyalikh, L. Bulusheva, Igor G. Chekhova and etc. // J. Phys. Chem. C 2013, 117, 7940-7948

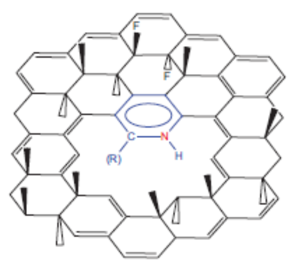
A. V. Okotrub, N. F. Yudanov, I. P. Asanov and etc. // ACSNano. 2013. V. 7 № 1. –P.65–74

T.L. Makarova, V.S. Zagaynova, G. Inan, A.V. Okotrub, G.N. Chekhova, D.V. Pinakov, L.G. Bulusheva //
J. Supercond Nov Magn. 2012. V. 25, № 1, p. 79-83.

$C_2F_{0.8} \cdot N_2O_4$

3) Substitution of Br_2 with CH_3CN until the liquid phase becomes discolored.





Yu. V. Fedoseeva,A.V.Okotrub, I. P.Asanov and etc.// Phys. Status Solidi B 251. 2014. No. 12, -P. 2530–2535

4) $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$

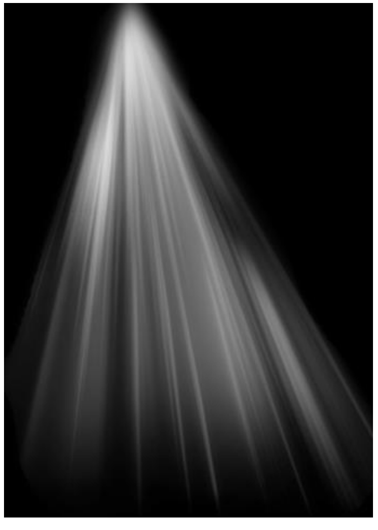
The **main goal** is to determine the mechanism of interaction of N_2O_4 with a matrix of semifluorinated graphite and related intermediate reaction products under the influence of external factors.

The **objective**: to carry out a detailed investigation of the electronic structure of intercalated by N_2O_4 semifluorinated graphite $C_2F_{0.8}$ before and after thermal exposure and irradiation with zero-order light from synhrotron (the so-called "white light").

Experimental

FTIR spectra - Scimitar FTS 2000 spectrometer.
Thermal exposure - for **10** minutes at a temperature of **190-200** °C

The **XPS** and **NEXAFS** experiments for $\mathbf{C_2F_{0.8}\cdot N_2O_4}$ - monochromatized synchrotron radiation from the Russian–German beamline (RGBL) at BESSY II, Germany. Additional XPS studies were conducted at the Boreskov Institute of Catalysis on an ESCA-Specs spectrometer.



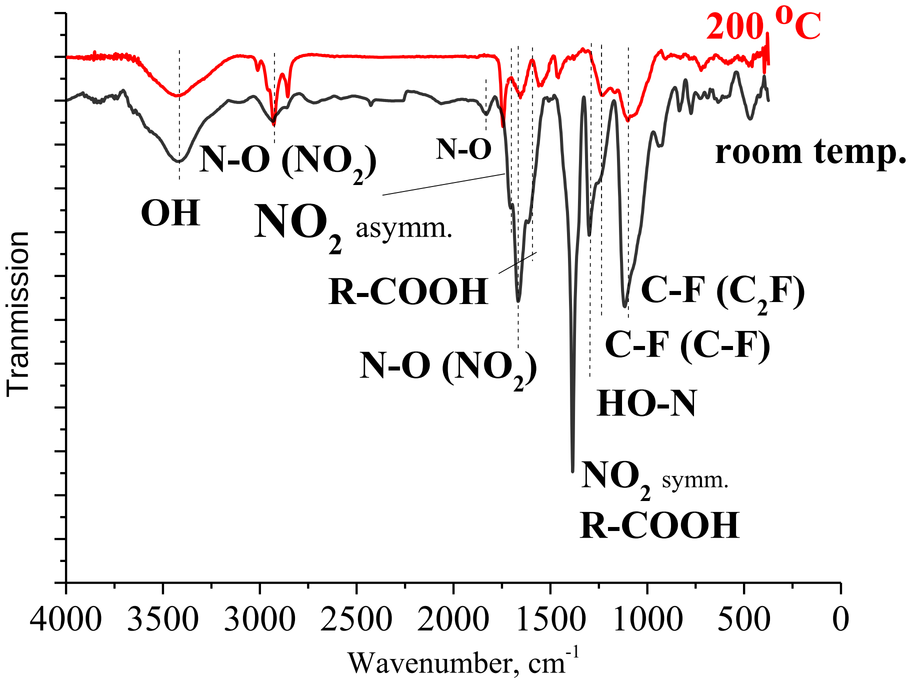
Influence with zero-order light illumination from the RGBL of BESSY II on the sample $C_2F_{0.8}\cdot N_2O_4$.

- Energy range 30-1300 eV.
- Total energy flow over all wavelengths $\Phi \approx 2\times10^{-3}$ J/s.
- Under illumination for 180 s. total energy $E_{tot} \approx 0.36$ J.
- Dose = 9×10^{5} J/kg.

The scheme of our experiment included:

1. Measurement of XPS and NEXAFS spectra of a sample.
2. Illumination of a sample by zero-order light for 180 seconds
3. Repeated measurement of the XPS and NEXAFS spectra.

Investigation of the effect of thermal exposure on $C_2F_{0.8} \cdot N_2O_4$ using IR spectroscopy



Structural fragments	wavenumber, $см^{-1}$	Ref.
C-F (C_2F)	1099	[1]
C-F (CF)	1234	[1]
HON (HNO_3)	1300	[2]
NO_2 (HNO_3)	1340 sym. 1709 asym.	[2]
R-COOH	1385 1600	[3]
C=C	1570	[4]
N-O (NO_2)	1660 2936	[5]
OH	3424	[2]

Possible chemical reactions, flowing on the surface $C_2F_{0.8}$:

- $NO_2 + NO_2 \rightarrow NO + NO_3$
- $2\ (NO_2 + NO) \rightarrow 2NO_3 + N2$
- $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

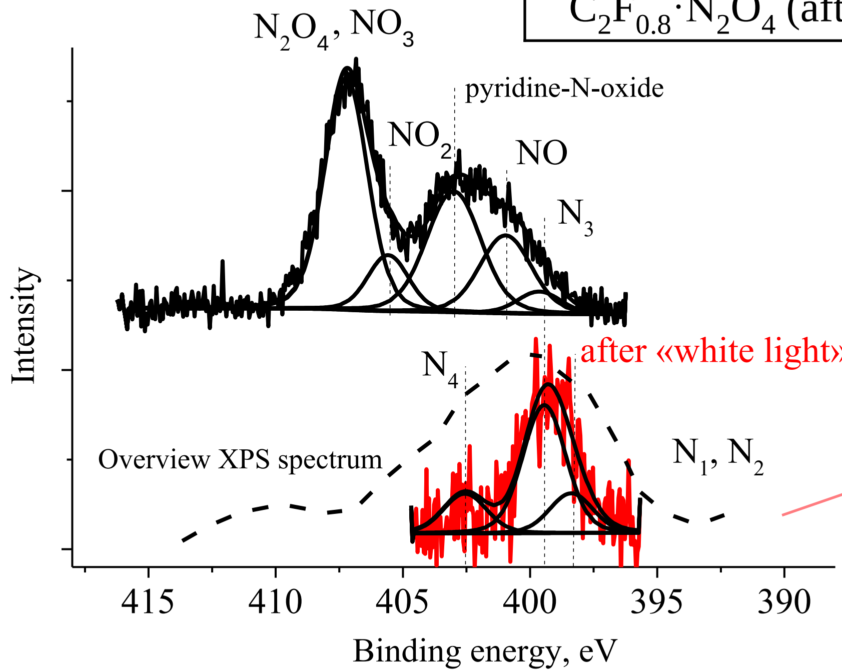
[1] Frantisek Karlick, Kasibhatta Kumara Ramanatha Datta, Michal Otyepka, and Radek Zboril. // ACS Nano. VOL. 7 ’ NO. 8 -2013. -P. 6434–6464.
[2] NIST Inorgenic Crystal Structure Database (ICSD) https://webbook.nist.gov
[3] Weikang Zhu, Xiangwen Zhang and etc. In-situ electrochemical activation of carbon fiber paper for the highly efficient electroreduction of concentrated nitric acid // Electrochimica Acta, 2018, 291. –P.328-334.
[4] M. Praveen Kumar, T. Kesavan, Golap Kalita, P. Ragupathy and etc . // RSC Adv., 2014, 4, 38689
[5] https://www.gasmet.com/products/tools/spectrum-library/nitrogen-dioxide/

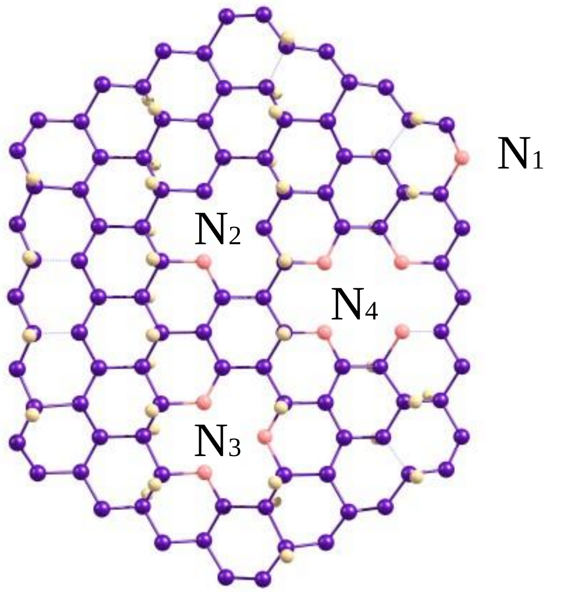
Investigation of the effect of thermal annealing and «white light» illumination on $C_2F_{0.8}\cdot N_2O_4$ using XPS

Elemental composition of the sample surface $C_2F_{0.8}\cdot N_2O_4$ before and after white light illumination for 180 sec.

Образец	C,%	F,%	N,%	O,%
$C_2F_{0.8}\cdot N_2O_4$ (before wh.light)	67,6	23,5	3,7	5,2
$C_2F_{0.8}\cdot N_2O_4$ (after wh.light)	85,4	8,5	2,1	4,0
$C_2F_{0.8}\cdot N_2O_4$ (after ther. an.)	85,1	5,7	-	9,2

XPS N(1s)

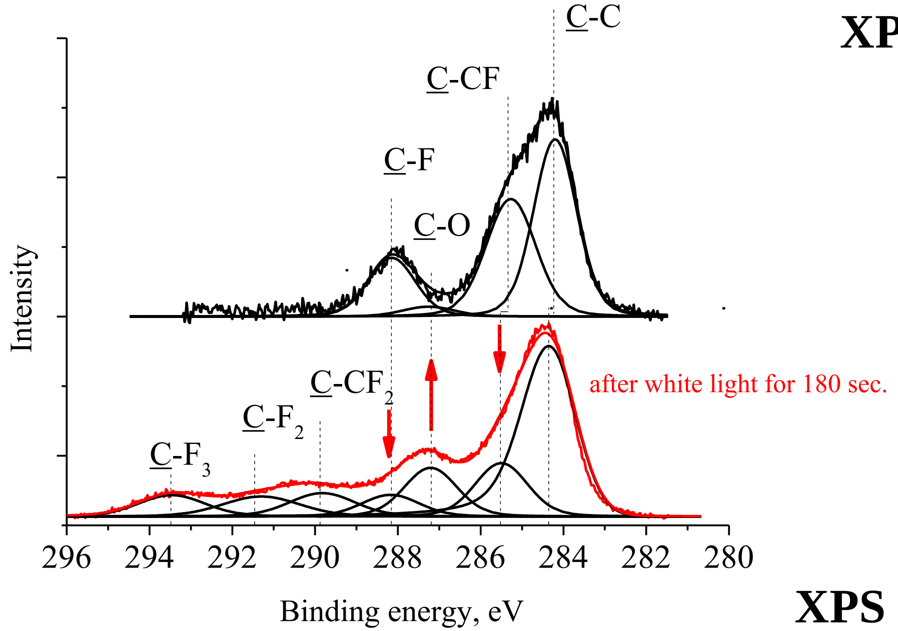


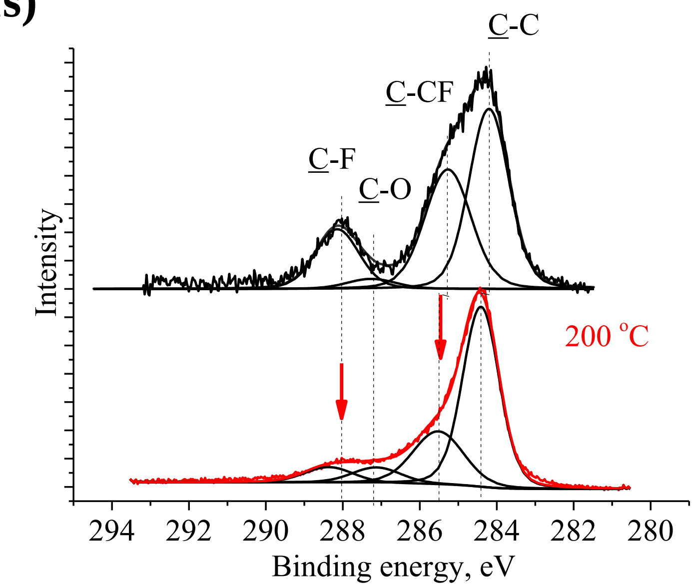


Thermal exposure **200 °C** for 10 minutes leads to the removal of nitrogen-containing functional groups from the surface $C_2F_{0.8-0.9}\cdot N_2O_4$

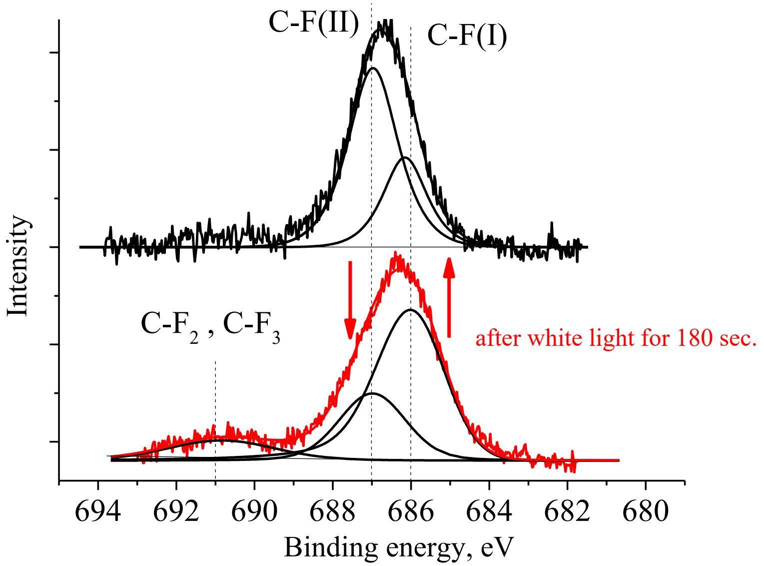
Investigation of the effect of thermal annealing and «white light» illumination on $C_2F_{0.8}{\cdot}N_2O_4$ using XPS

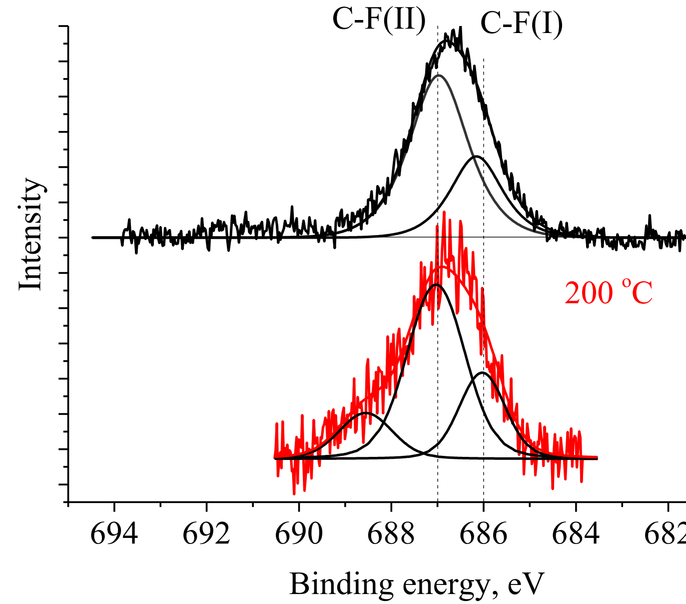
XPS C(1s)



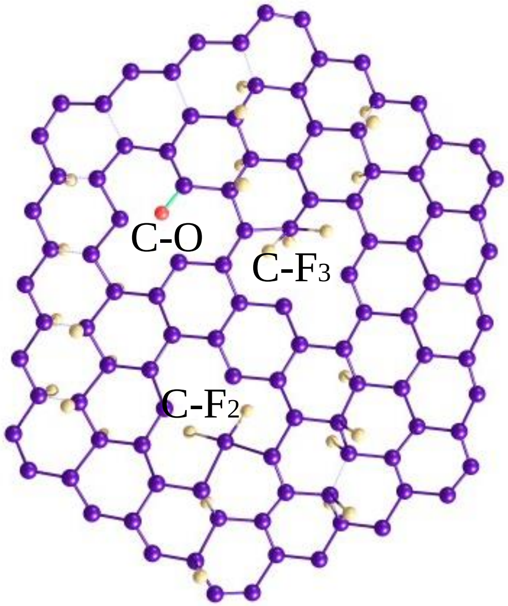


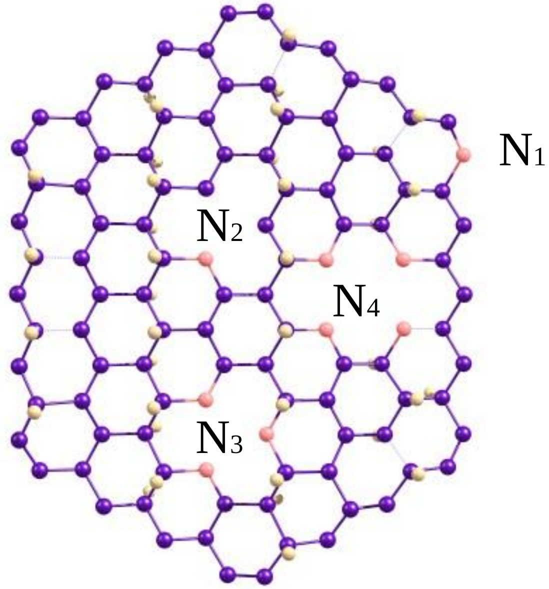
XPS F(1s)



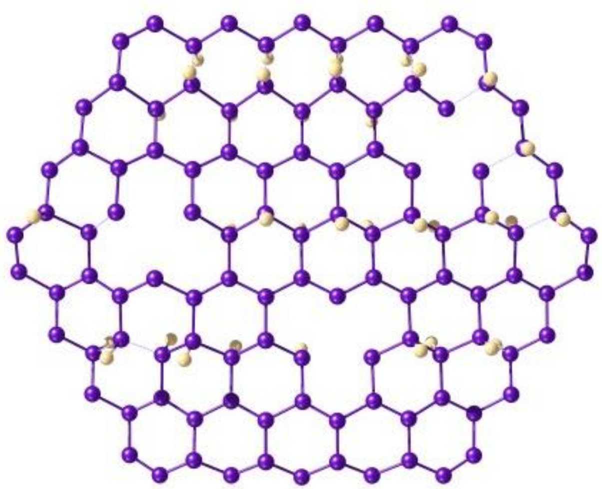


The effect of «white light» exposure on surface $C_2F_{0.8}\cdot N_2O_4$ for 180 sec.



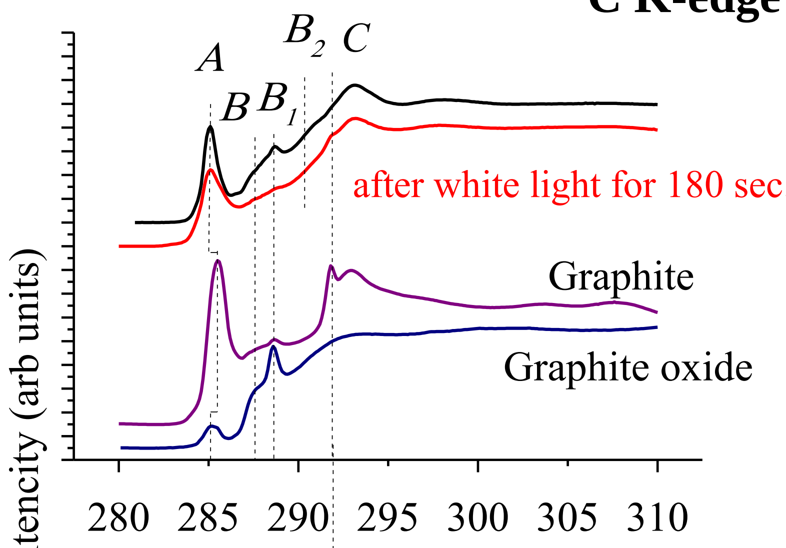


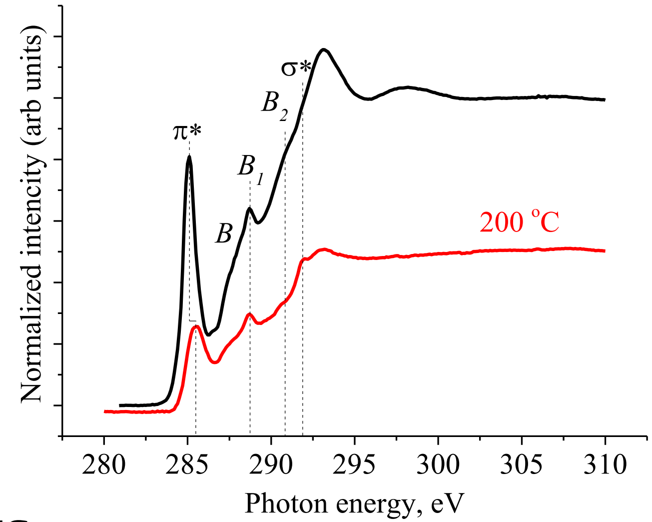
The effect of thermal exposure (200 ºC) on surface $C_2F_{0.8}\cdot N_2O_4$ for 10 minutes



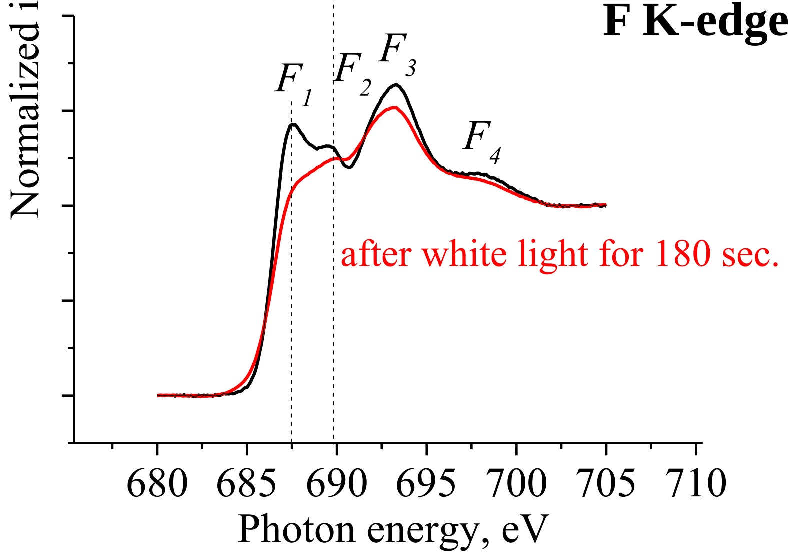
Investigation of the effect of thermal and «white light» exposure on $C_2F_{0.8}\cdot N_2O_4$ by NEXAFS

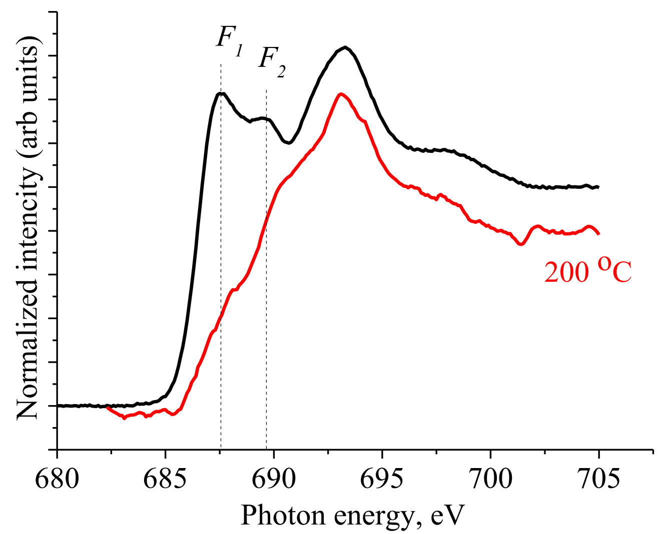
C K-edge NEXAFS





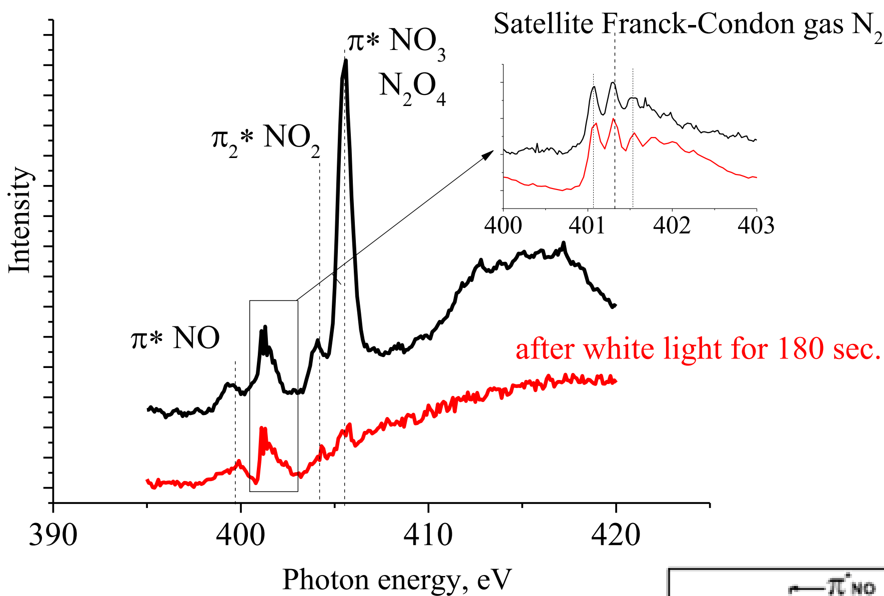
F K-edge NEXAFS

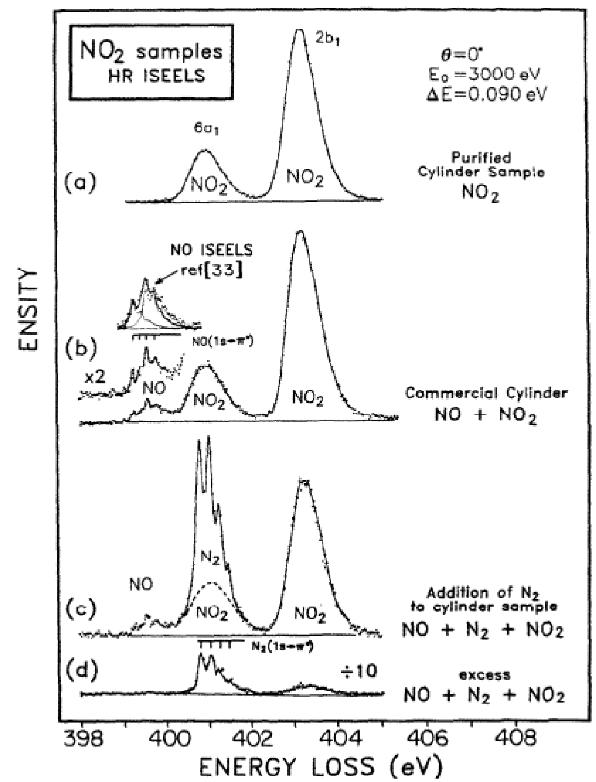




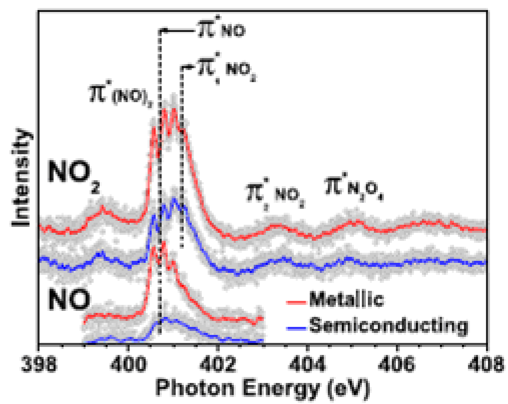
Investigation of the effect of thermal and «white light» exposure on $C_2F_{0.8}\cdot N_2O_4$ by NEXAFS

N K-edge NEXAFS

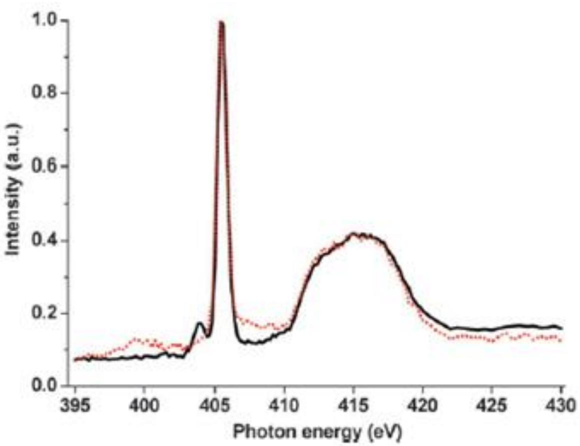




Investigation of sample purity in NO_2 cylinders by high-resolution ISEELS measuremeats in the N 1s region: (a) purified NO_2; (b) cylinder NO_2 (unpurified) showing NO impurity and the high-resolution NO spectrum; (c) Addition of N_2 to cylinder NO_2; (d) Same as (c) but with excess N_2[W. ZHANG, K.H. SZE, C.E. BRION // Chemical Physics 140 (1990) 265-279].

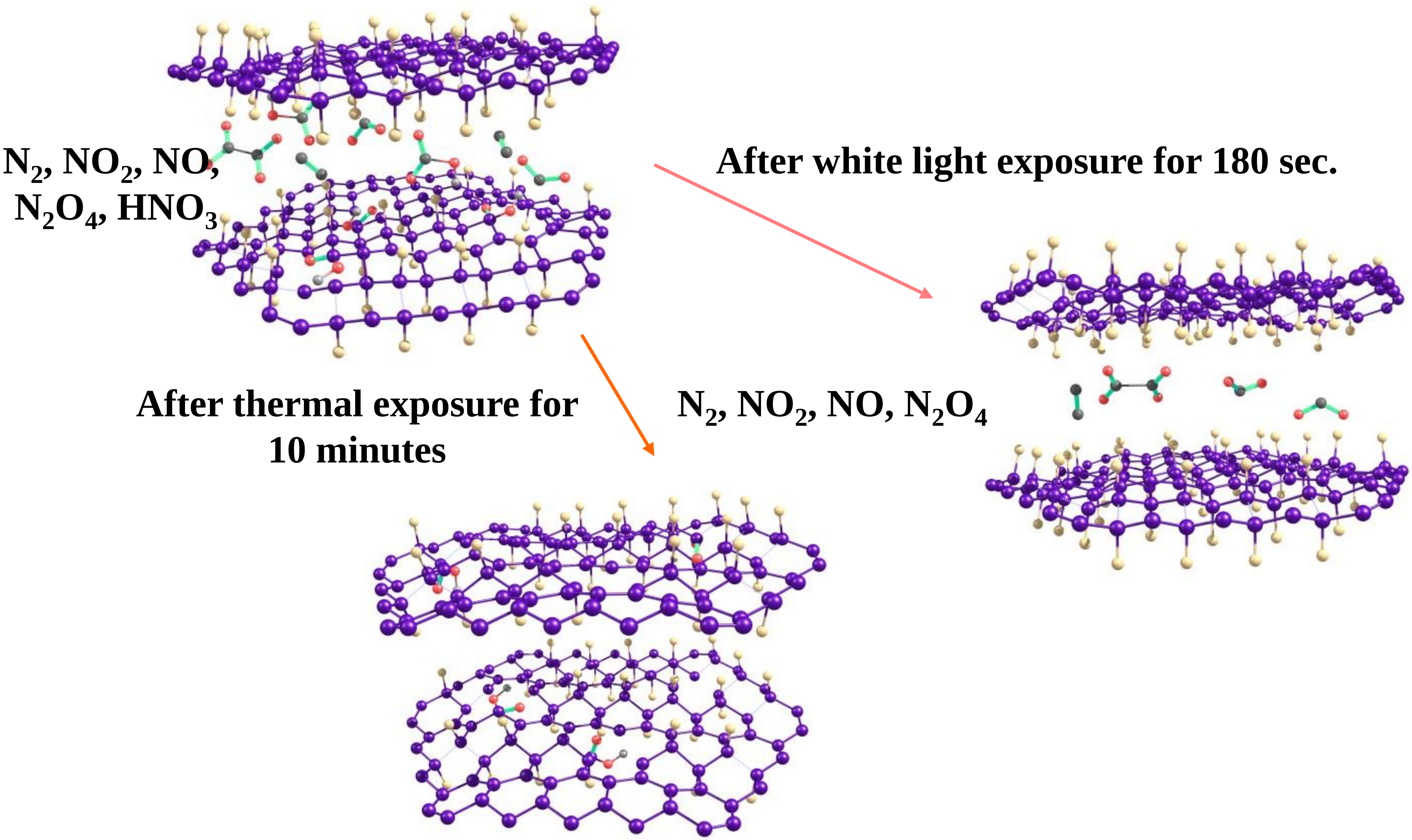


N K-edge_XANES NO_2 и NO, adsorbed on a carbon nanotube [Georgina Ruiz-Soria, Alejandro Perez Paz, Markus Sauer and etc. // ACSnano. -2014.V. 8, № 2. –P. 1375–1383.]



N K-edge NEXAFS of ice with HNO_3 [A. Krepelova, J. Newberg, T. Huthwelker and etc.// Phys. Chem. Chem. Phys., 2010, 12, 8870–8880].

The effect of thermal and «white light» exposure on bulk $C_2F_{0.8} \cdot N_2O_4$



Conclusions

1. The fluorinated graphite matrix can be used as a nanoreactor. Substitution of intercalate - acitonitrile with nitrogen tetroxide, which is in equilibrium with nitrogen dioxide, leads to the formation of nitrogen-containing molecules HNO_3, NO, N_2 in the interlayer space $C_2F_{0.8}$.
2. The effect of the zero-order beam from RGBL BESSY II exposure on the $C_2F_{0.8} \cdot N_2O_4$ sample for 180 seconds leads to partial defluorination of the sample with the possible removal of carbon and the formation of vacancy defects. At the edge of the fluorine graphite plane, the formation of the C-F_2, C-F_3, C-O bond occurs and included pyridine groups are observed.
3. It was found that by thermal shock HNO_3 is removed from the semifluorinated graphite matrix with the preservation of the remaining nitrogen-containing intercalate groups: NO, NO_2, N_2, N_2O_4.
4. Annealing at ~ 200 °C of sample $C_2F_{0.8} \cdot N_2O_4$ for 10 minutes facilitates the production of an “empty” matrix with partial defluorination and the formation of vacancy defects.

This work was supported by RFBR grant № 18-29-19073 мк.

THANKS FOR ATTENTION !!!