

Characterization of Complex Interactions at the Gas-Solid Interface with *In Situ* Spectroscopy: The Case of Nitrogen-Functionalized Carbon

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Supporting Information

Elemental Composition (at. %)

Sample ID	C - EDS	C - XPS	O - EDS	O - XPS	N - EDS	N - XPS
N-C_{sph} 600 °C	96.5	92.7	1.6	4.1	1.9	3.1
N-C_{sph} 700 °C	96.7	93.3	1.5	3.6	1.9	3.0
N-C_{sph} 900 °C	96.8	94.9	1.5	3.1	1.8	2.0
N-Vulcan	98.8	96.8	0.6	2.4	0.6	0.9
N-GnP	98.7	87.7	0.6	6.2	0.8	6.1

Table S1: Elemental compositions of all N-C samples obtained from EDS and XPS are displayed as atomic percentages.

N 1s Fitting Parameters - UHV

N Species	Electron-rich						Amine		Hydrogenated (in-plane)				Graphitic				Hydrogenated (edge)	
	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit
N-C_{sph} 600 °C	397.6	3.7	398.1	28.0	398.7	12.7	399.5	11.0	400.1	16.2	400.6	20.5	401.2	5.7	402.0	2.2	X	0.0
N-C_{sph} 700 °C	397.6	7.4	398.0	20.4	398.7	11.4	399.4	10.7	400.1	16.7	400.7	22.4	401.4	8.6	402.0	2.5	X	0.0
N-C_{sph} 900 °C	397.6	1.0	398.0	18.4	398.7	9.4	399.3	6.9	400.1	14.8	400.7	30.7	401.4	14.1	402.0	4.6	X	0.0
N-Vulcan	X	0.0	398.0	3.3	398.8	16.4	399.3	10.8	399.9	22.9	400.6	22.8	401.3	15.8	402.1	5.4	402.8	2.6
N-GnP	X	0.0	398.2	8.1	398.7	18.4	399.4	23.0	400.0	22.2	400.6	17.5	401.2	8.0	402.2	3.0	X	0.0

Table S2: Fitting parameters (BE and relative percentage of the fit) of the N 1s measured at UHV and ambient temperature are displayed for all components of all samples. Components that are not present in a sample are denoted with an X in the BE column. The FWHM of all components is 1.0 eV.

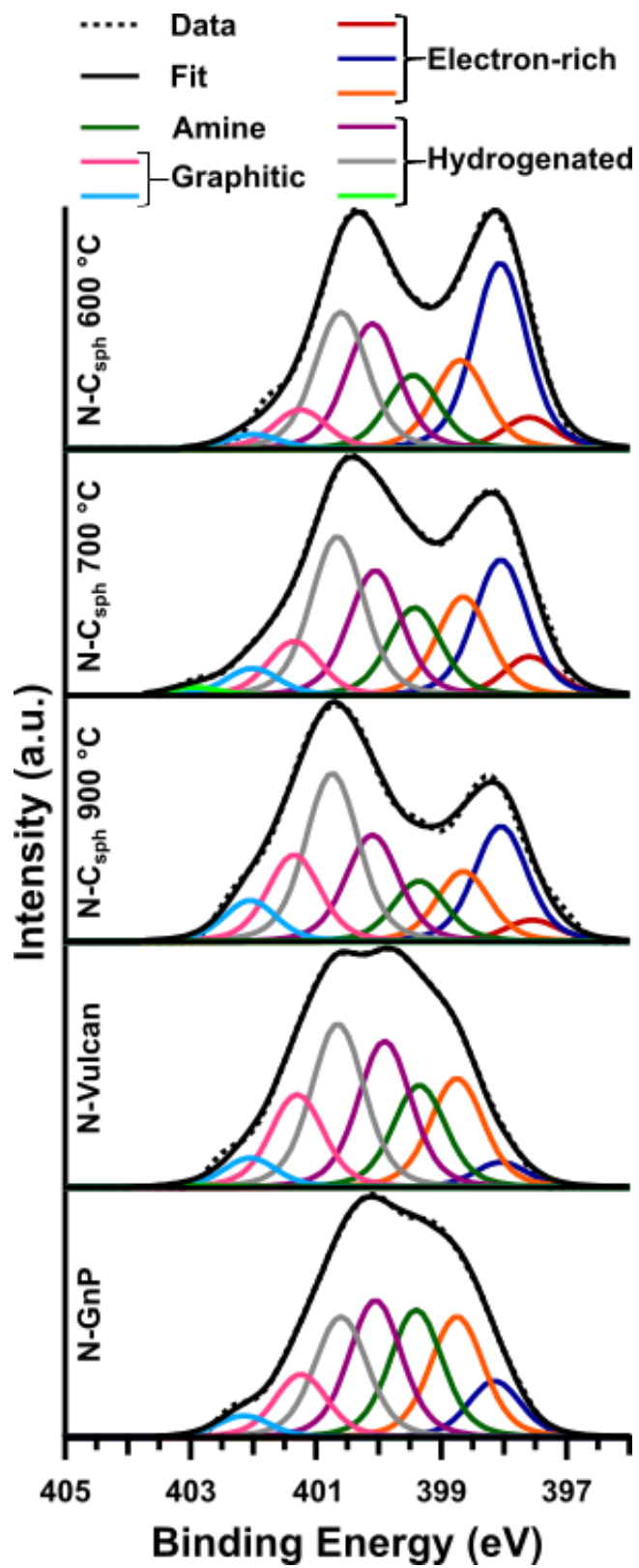


Figure S1: Deconvoluted N 1s spectra collected with synchrotron source energy (630 eV) at 100 mTorr O₂ at 60 °C are shown for all N-C materials.

N 1s Fitting Parameters – O₂; 60 °C

Component	Electron-rich						Amine		Hydrogenated (in-plane)				Graphitic				Hydrogenated (edge)	
	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit
N-C_{sph} 600 °C	397.6	4.5	398.1	26.8	398.7	12.8	399.5	10.5	400.1	17.9	400.6	19.7	401.3	5.7	402.0	2.1	X	0.0
N-C_{sph} 700 °C	397.6	5.3	398.1	18.5	398.7	13.4	399.4	11.9	400.1	17.1	400.7	21.8	401.4	7.3	402.0	3.7	403.0	1.1
N-C_{sph} 900 °C	397.6	3.2	398.1	17.3	398.7	10.5	399.4	9.0	400.1	16.0	400.7	25.2	401.4	12.8	402.1	6.1	X	0.0
N-Vulcan	X	0.0	398.1	3.7	398.8	16.4	399.4	15.2	399.9	21.9	400.7	24.4	401.3	13.8	402.1	4.4	402.8	0.3
N-GnP	X	0.0	398.2	8.7	398.8	18.8	399.4	19.7	400.1	21.1	400.6	18.7	401.2	9.7	402.2	3.3	X	0.0

Table S3: Fitting parameters (BE and relative percentage of the fit) of the N 1s measured in 100 mTorr of O₂ at 60 °C are displayed for all components of all samples. Components that are not present in a sample are denoted with an X in the BE column. The FWHM of all components is 1.0 eV.

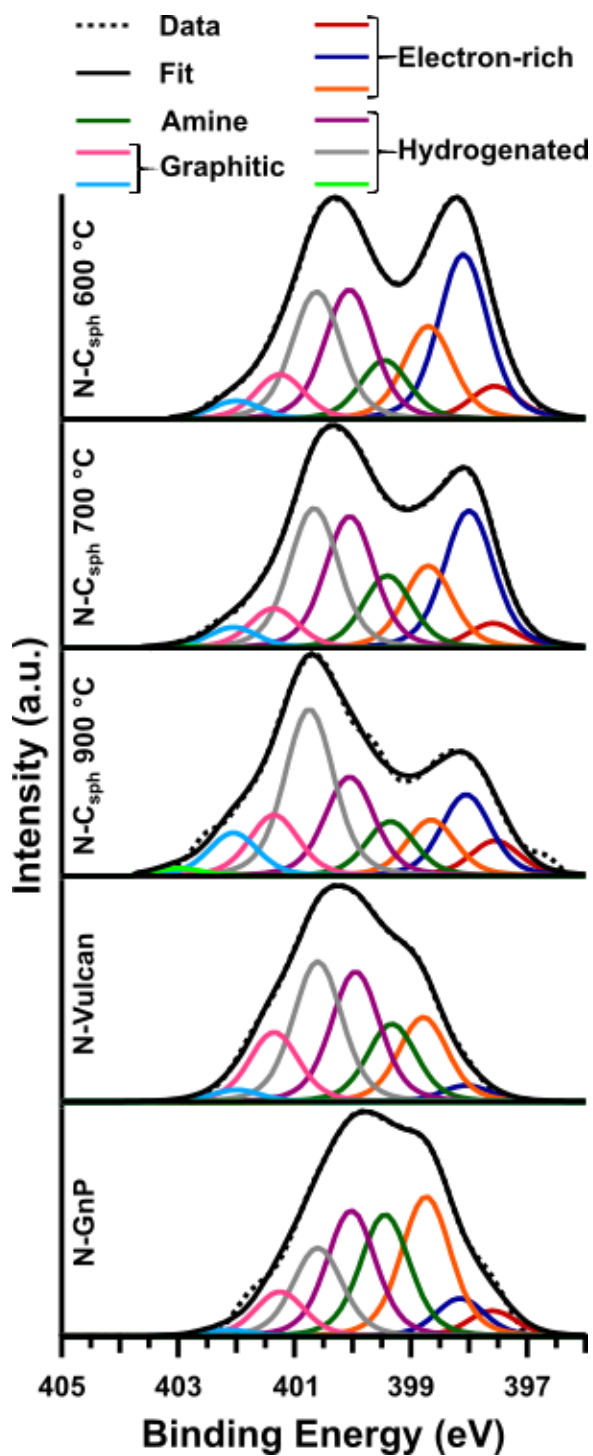


Figure S2: Deconvoluted N 1s spectra collected with synchrotron source energy (630 eV) at 100 mTorr O₂ and 100 mTorr H₂O at 60 °C are shown for all N-C materials.

N 1s Fitting Parameters – O₂ + H₂O; 60 °C

Component	Electron-rich						Amine		Hydrogenated (in-plane)				Graphitic				Hydrogenated (edge)	
	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit	BE	% of Fit
N-C_{sph} 600 °C	397.6	4.9	398.1	24.6	398.7	13.9	399.5	8.8	400.1	19.4	400.6	18.9	401.3	6.7	402.0	2.8	X	0.0
N-C_{sph} 700 °C	397.6	3.8	398.0	21.2	398.7	12.6	399.4	11.1	400.1	20.3	400.7	21.6	401.4	6.0	402.1	3.2	403.0	0.3
N-C_{sph} 900 °C	397.6	5.8	398.1	13.5	398.7	9.2	399.4	9.0	400.1	16.5	400.7	27.5	401.4	10.1	402.1	7.2	403.0	1.3
N-Vulcan	X	0.0	398.1	3.1	398.8	15.9	399.3	14.7	400.0	24.5	400.6	26.4	401.4	13.2	402.0	2.2	X	0.0
N-GnP	397.6	4.3	398.2	6.4	398.7	23.8	399.4	20.7	400.0	21.2	400.6	15.0	401.3	7.6	402.2	1.1	X	0.0

Table S4: Fitting parameters (BE and relative percentage of the fit) of the N 1s measured in 100 mTorr each of O₂ and H₂O at 60 °C are displayed for all components of all samples. Components that are not present in a sample are denoted with an X in the BE column. The FWHM of all components is 1.0 eV.

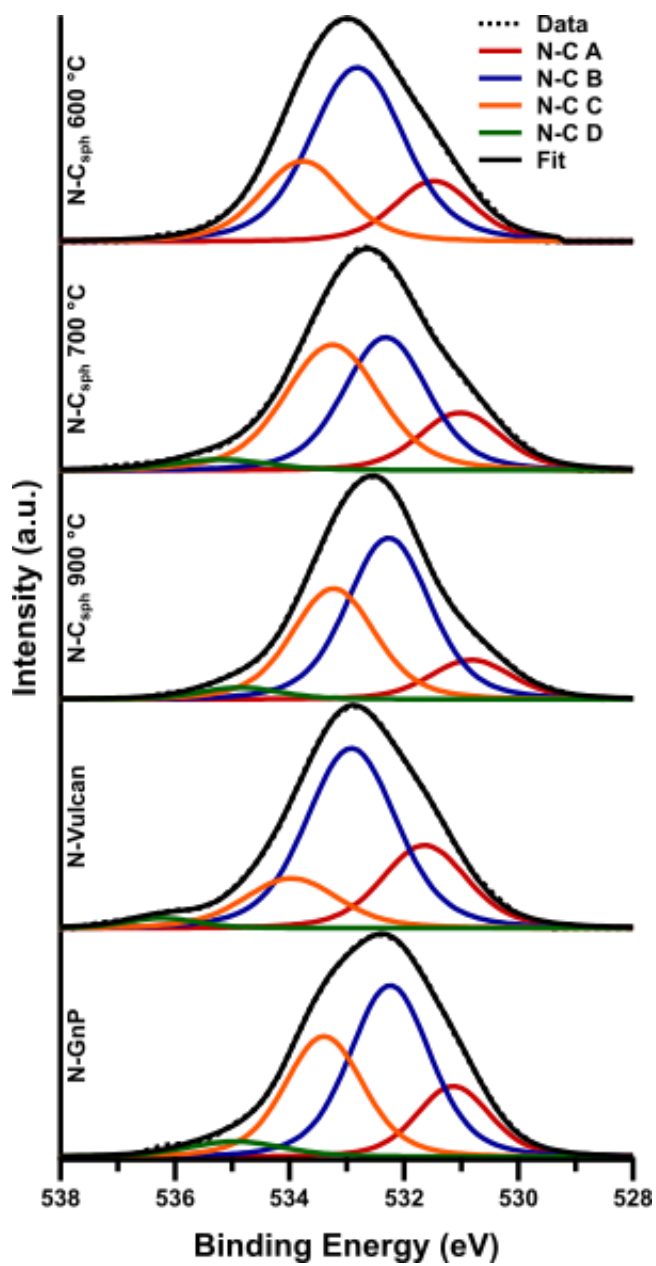


Figure S3: Deconvoluted O 1s spectra collected with synchrotron source energy (630 eV) at UHV are shown for all N-C materials.

O 1s Fitting Parameters - UHV

Component	N-C A			N-C B			N-C C			N-C D		
	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit
N-C_{sph} 600 °C	531.5	1.6	17.2	532.8	1.9	58.4	533.8	1.7	24.4	X	0.0	0.0
N-C_{sph} 700 °C	531.0	1.7	16.4	532.3	1.7	38.8	533.3	1.9	41.2	535.2	2.0	3.6
N-C_{sph} 900 °C	530.8	1.7	12.0	532.3	1.7	50.0	533.2	1.7	34.4	534.9	1.7	3.6
N-Vulcan	531.6	1.7	24.6	532.9	1.8	56.5	534.0	1.9	16.4	536.2	1.5	2.5
N-GnP	531.1	1.5	17.3	532.2	1.6	46.1	533.4	1.6	31.6	535.0	2.0	5.0

Table S5: Fitting parameters (BE, FWHM in eV, and relative percentage of the fit) of the O 1s measured at UHV and ambient temperature are displayed for all components of all samples.

Components that are not present in a sample are denoted with an X in the BE column.

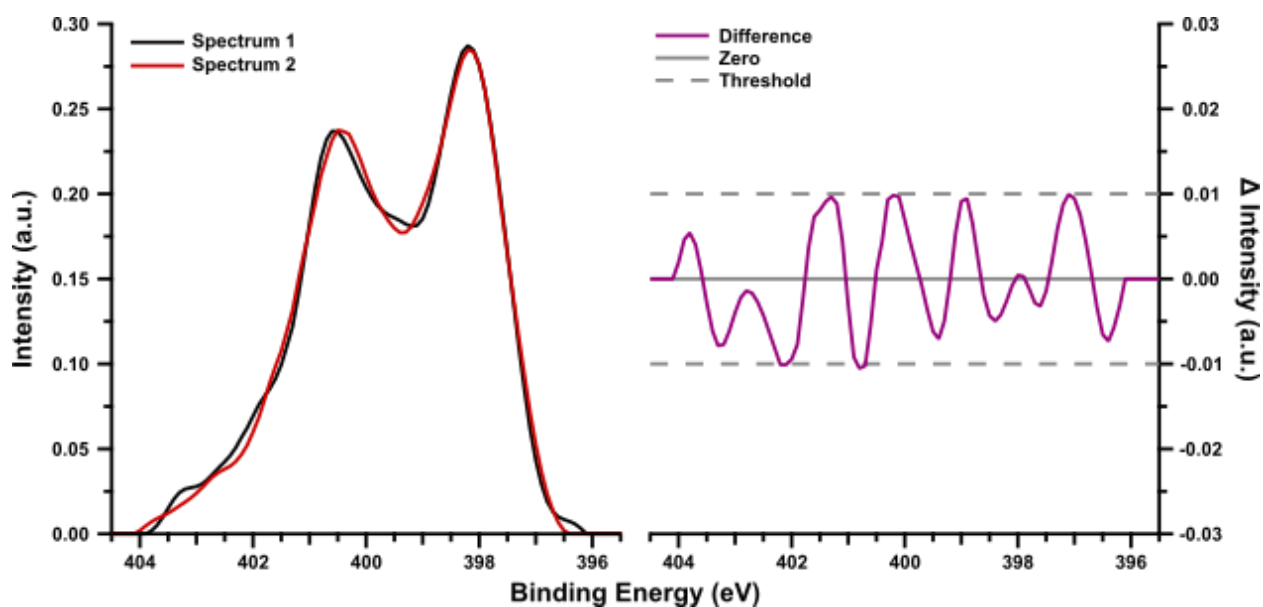


Figure S4: Overlaid N 1s spectra taken with the exact same conditions are shown along with the difference spectrum in order to validate the use of a threshold to remove instrumental noise.

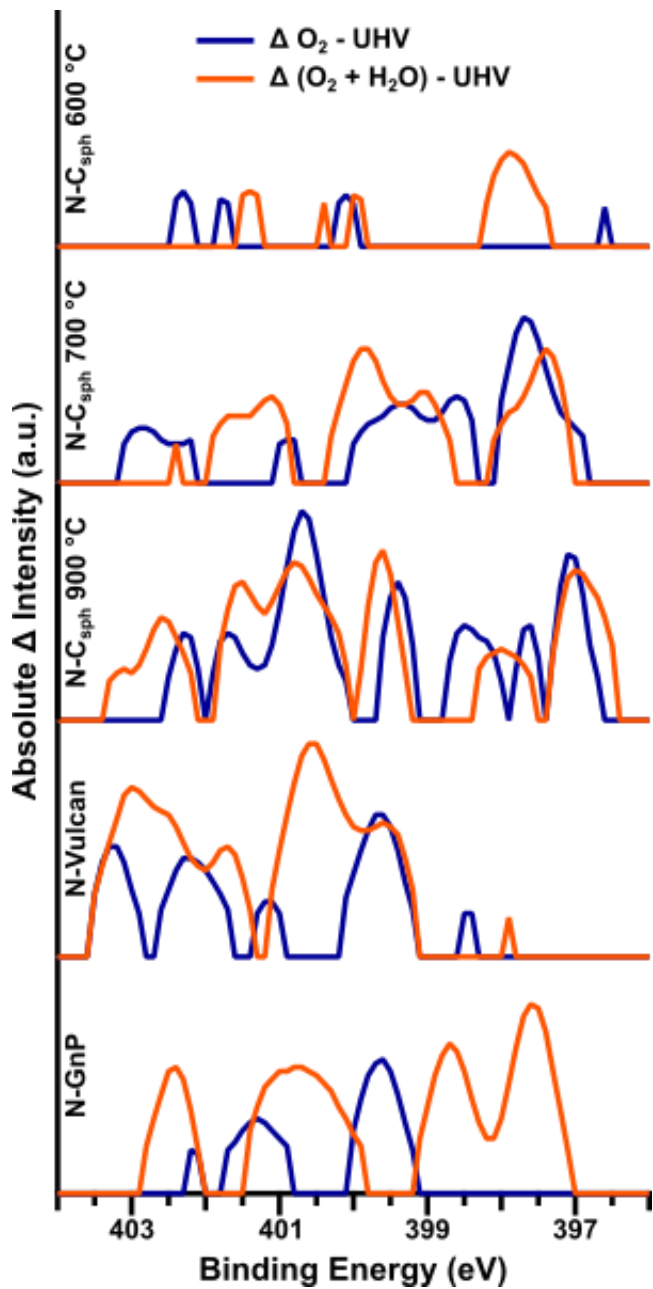


Figure S5: Absolute N 1s difference spectra are shown for each atmosphere, relative to UHV measurements and after thresholding. These spectra are integrated to produce a value for the total change in N 1s.

O 1s Fitting Parameters – O₂; 60 °C

Component	N-C A			N-C B			N-C C			N-C D			O _{ads}			O ₂ (v) 1			O ₂ (v) 2		
	Sample ID	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM
N-C _{sph} 600 °C	531.5	1.6	8.4	532.8	1.9	28.5	533.8	1.7	11.9	X	0.0	0.0	530.6	1.0	0.8	538.6	0.8	34.5	539.7	0.9	15.9
N-C _{sph} 700 °C	531.0	1.7	9.1	532.3	1.7	21.4	533.3	1.9	22.7	535.2	2.0	2.0	533.6	2.0	2.2	538.7	0.8	29.9	539.8	0.8	12.7
N-C _{sph} 900 °C	530.8	1.7	4.9	532.3	1.7	20.3	533.2	1.7	13.9	534.9	1.7	1.5	534.0	1.8	3.1	538.7	0.7	38.3	539.8	0.8	18.2
N-Vulcan	531.6	1.7	7.5	532.9	1.8	17.3	534.0	1.9	5.0	536.2	1.5	0.8	533.6	1.0	1.4	538.9	0.8	46.7	540.0	0.8	21.3
N-GnP	531.1	1.5	6.9	532.3	1.6	18.5	533.4	1.6	12.7	535.0	2.0	2.0	534.4	1.2	0.8	538.7	0.8	39.6	539.9	0.9	19.5

Table S6: Fitting parameters (BE, FWHM in eV, and relative percentage of the fit) of the N 1s measured in 100 mTorr of O₂ at 60 °C are displayed for all components of all samples.

Components that are not present in a sample are denoted with an X in the BE column.

O 1s Fitting Parameters – O₂ + H₂O; 60 °C

Component	N-C A			N-C B			N-C C			N-C D			O _{ads}			O ₂ (v) 1			O ₂ (v) 2			H ₂ O (v)		
	Sample ID	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM	% of fit	BE	FWHM
N-C _{sph} 600 °C	531.5	1.6	7.4	532.8	1.9	25.2	533.8	1.7	10.5	X	0.0	0.0	530.6	1.1	1.4	538.6	0.8	23.1	539.8	0.9	10.0	535.2	0.8	22.4
N-C _{sph} 700 °C	531.0	1.7	6.9	532.3	1.7	16.3	533.3	1.9	17.3	535.2	2.0	1.5	533.1	1.1	2.3	538.6	0.8	22.7	539.8	0.8	9.9	535.2	0.8	23.1
N-C _{sph} 900 °C	530.8	1.7	3.6	532.3	1.7	14.9	533.2	1.7	10.3	534.9	1.7	1.1	533.7	2.1	3.1	538.8	0.7	27.7	539.9	0.8	12.8	535.3	0.8	26.6
N-Vulcan	531.7	1.7	4.8	532.9	1.8	11.0	534.0	1.9	3.2	536.2	1.5	0.5	533.6	1.0	2.6	538.9	0.8	32.2	540.1	0.8	14.3	535.5	0.8	31.4
N-GnP	531.2	1.5	4.5	532.2	1.6	11.9	533.4	1.6	8.1	535.0	2.0	1.3	532.7	1.5	4.3	538.8	0.8	28.4	539.9	0.9	13.2	535.3	0.8	28.3

Table S7: Fitting parameters (BE, FWHM in eV, and relative percentage of the fit) of the O 1s measured in 100 mTorr each of O₂ and H₂O at 60 °C are displayed for all components of all samples. Components that are not present in a sample are denoted with an X in the BE column.