Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Influence of TiO_2 Surface Defects on the Adsorption of N719 Dye Molecules

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SUPPORTING INFORMATION:

NICISS results.

NICIS spectra of TiO_2 samples before and after immersion in N719 dye is plotted against the TOF are shown in Figure S 1.

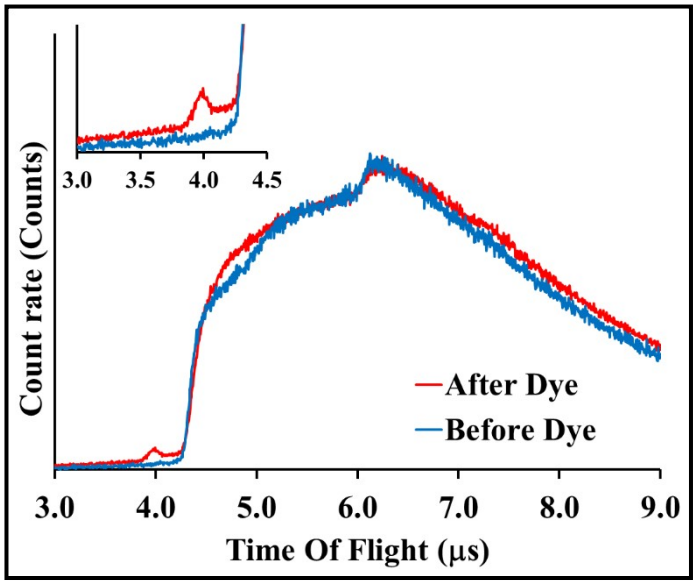

Figure S 1: NICIS spectra of TiO_2 before and after immersion into a N719 dye solution. The inset shows the peak at ~4 µs originating from Ru.

The features in the TOF spectra can be assigned to titanium (4.5 µs), oxygen (6.4 µs), and carbon (7.4 µs). After the TiO_2 samples had been immersed into a N719 dye solution, a very broad and intense signal appeared at ~ 4 µs attributed to Ru adsorbed on the sample.

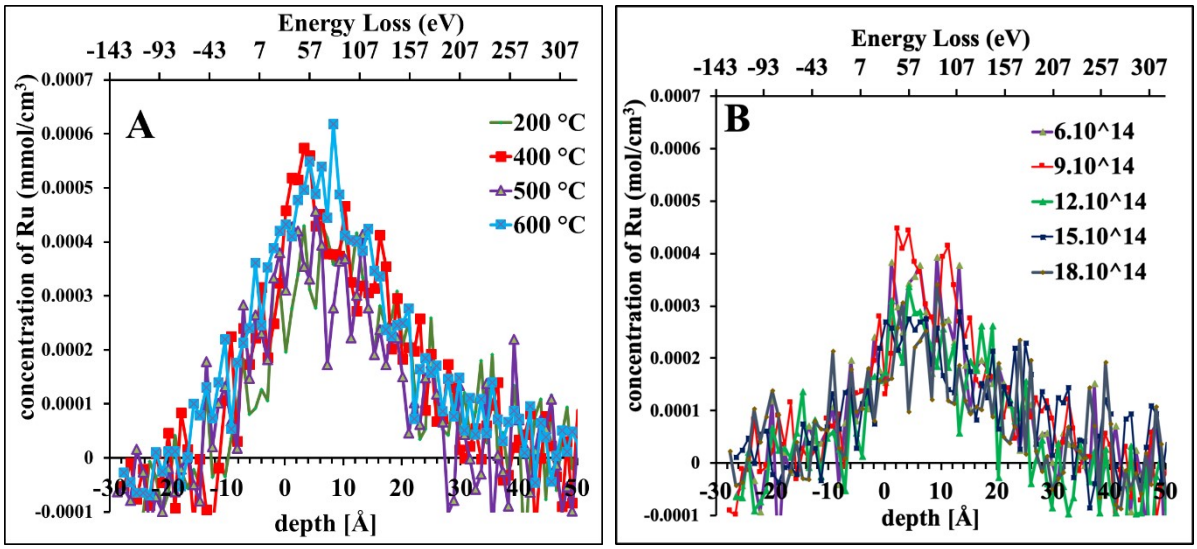

Figure S 2: Concentration depth profile of the dye N719 on A) pre-heated TiO_2 surface and B) pre-heated/sputtered TiO_2 surface. For explanation of the meaning of the two abscissas at the top and bottom, see Figure 1.

XPS results.

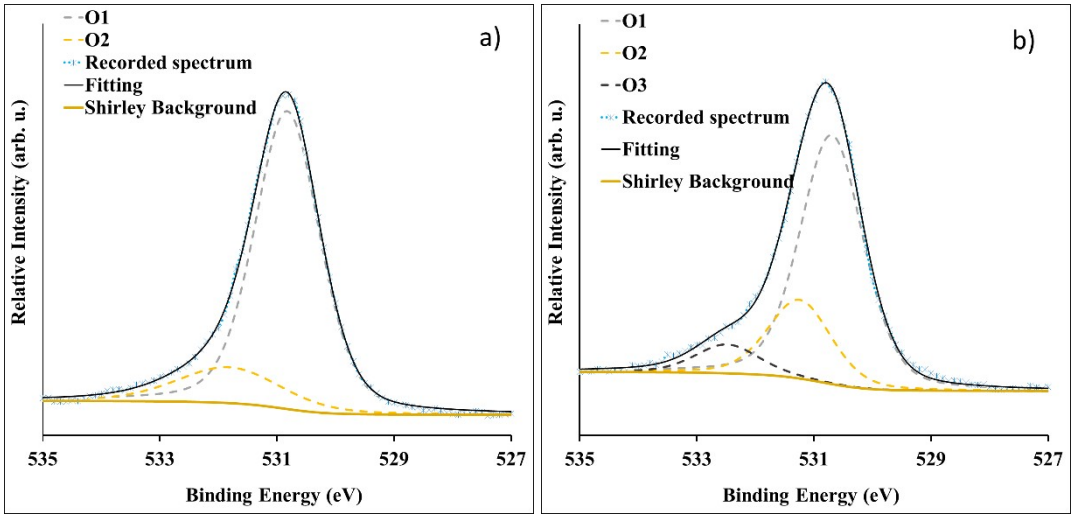

Figure S 3: XP spectra of O 1s an untreated TiO_2 sample a) before and b) after N719 deposition. It should be noted that for the untreated sample the amount of N719 adsorbed to the sample was so small that no discernible S peak could be identified within the noise of the data.

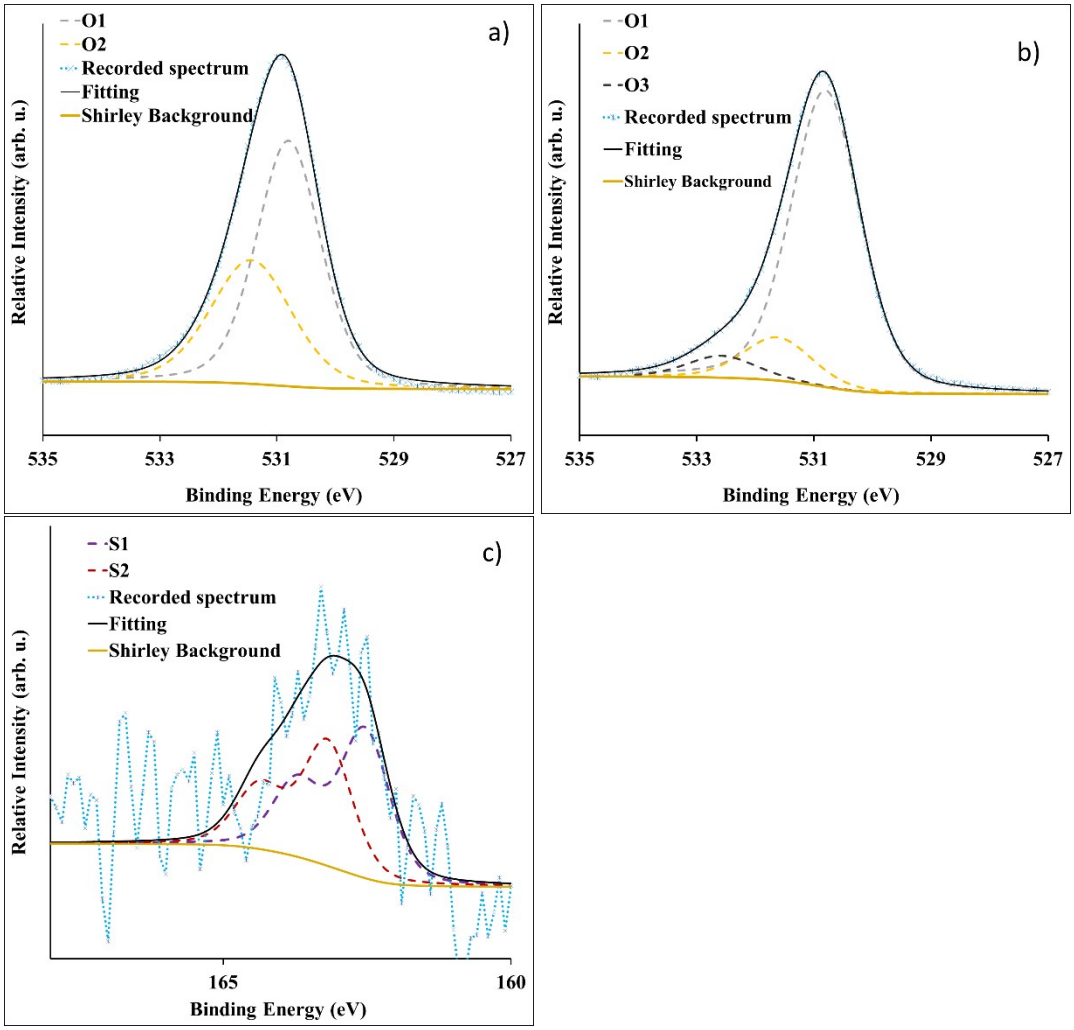

Figure S 4: XP spectra of O 1s a pre-heated/sputtered TiO_2 sample ($18 \cdot 10^{14}$ ions/cm^2) a) before and b) after N719 deposition and c) S 2p after deposition of N719.

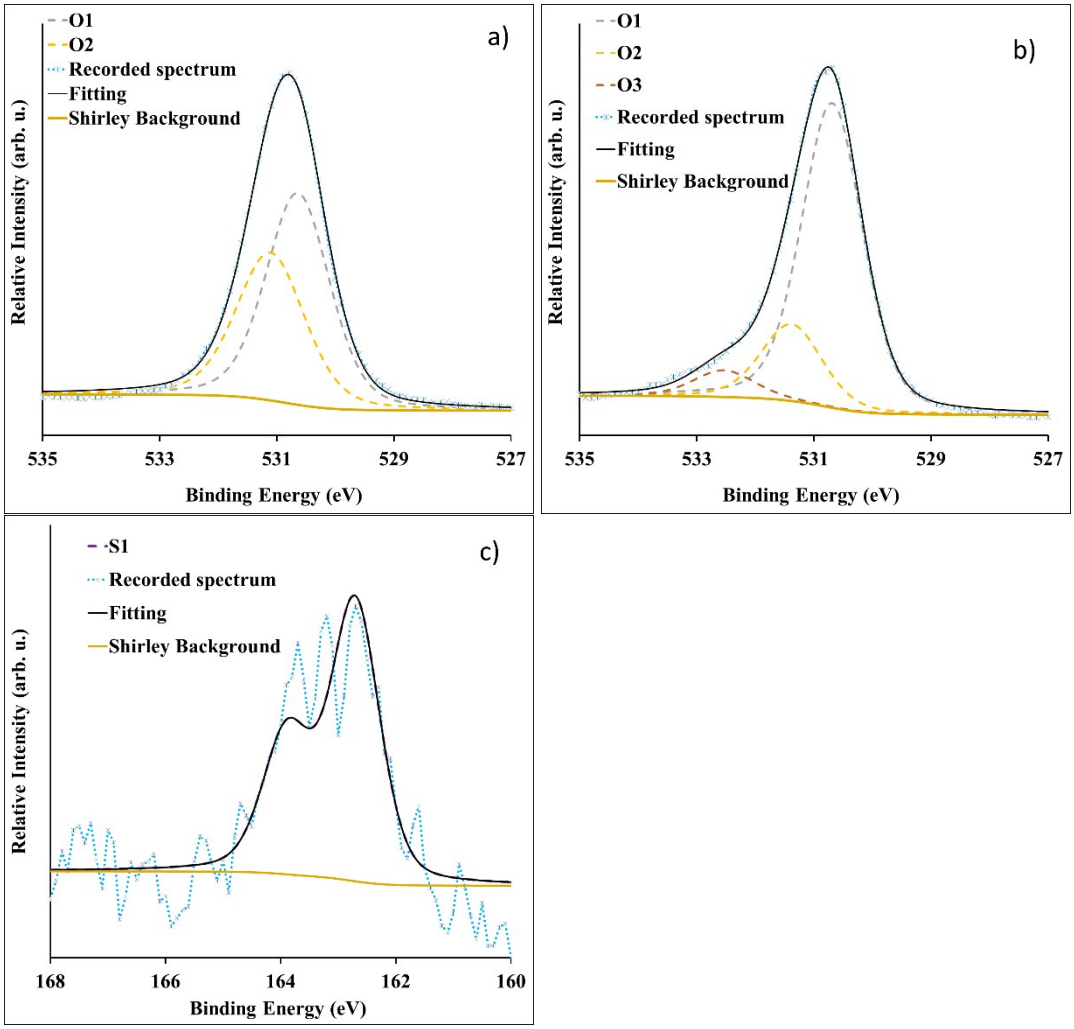

Figure S 5: XP spectra of O 1s a pre-heated TiO_2 sample (600°C) a) before and b) after N719 deposition and c) S 2p after deposition of N719.

Table S1. Peak positions ± 0.2 eV and the relative peak intensities ± 0.3 % for the ascending temperature pre-treated TiO_2 samples (pre-heated samples).

Element/Temperature		Untreated	200°C	400 °C	500°C	600°C
C1	**Position**	**285.0**	**285.0**	**285.4**	**285.0**	**285.0**
	intensity%	**8.7**	**5.6**	**11.3**	**12.2**	**12.4**
C2	**Position**	**286.1**	**285.9**	**286.6**	**286.2**	**286.2**
	intensity %	**7.4**	**9.7**	**4.6**	**4.6**	**5.8**
C3	**Position**	**288.8**	**289.1**	**289.0**	**288.9**	**288.9**
	intensity %	**2.2**	**1.4**	**2.8**	**2.2**	**1.9**
O1	**Position**	**530.3**	**530.4**	**530.6**	**530.2**	**530.2**
	intensity %	**42.0**	**48.4**	**48.2**	**43.4**	**48.2**
O2	**Position**	**530.9**	**531.1**	**531.3**	**530.9**	**531.1**
	intensity %	**13.3**	**7.4**	**6.3**	**11.0**	**6.0**
O3	**Position**	**532.1**	**532.2**	**532.2**	**532.0**	**532.1**
	intensity %	**4.9**	**4.8**	**4.2**	**3.8**	**3.5**
Ti (Ti^{4+})	**Position**	**459.2**	**459.2**	**459.4**	**459.0**	**459.0**
	intensity %	**19.2**	**19.5**	**18.4**	**18.7**	**18.6**
Ru	**Position**	**281.3**	**281.3**	**281.5**	**281.0**	**281.1**
	intensity %	**0.16**	**0.26**	**0.29**	**0.30**	**0.29**
N_{pyd}	**Position**	**400.4**	**400.4**	**400.1**	**400.2**	**400.2**
	intensity %	**1.6**	**1.6**	**2.3**	**1.9**	**1.9**
N_{NCS}	**Position**	**398.6**	**398.4**	**398.0**	**397.9**	**398.1**
	intensity %	**0.5**	**0.8**	**0.9**	**0.9**	**0.8**
N_{TBA}	**Position**	**0.0**	**401.6**	**0.0**	**402.3**	**402.3**
	intensity %	**0.0**	**0.0**	**0.0**	**0.2**	**0.2**
S	**Position**	**0.0**	**161.7**	**162.1**	**162.2**	**162.0**
	intensity %	**0.0**	**0.4**	**0.7**	**0.8**	**0.4**

Table S2. Peak positions ± 0.2 eV and the relative peak intensities ± 0.3 % for the Ar^+ sputtered pre-treated TiO_2 samples at different doses (pre-heated/sputtered samples).

Element/Dose [ions/cm^2]		$6 \cdot 10^{14}$	$9 \cdot 10^{14}$	$12 \cdot 10^{14}$	$15 \cdot 10^{14}$	$18 \cdot 10^{14}$
C1	Position	285.3	285.0	285.0	285.3	285.0
	intensity %	9.2	8.2	7.7	6.7	5.3
C2	Position	286.4	286.1	286.2	286.5	286.2
	intensity %	6.1	6.6	3.6	3.1	5.1
C3	Position	289.2	289.0	289.0	289.4	289.4
	intensity %	1.3	1.3	1.4	0.9	0.9
O1	Position	530.6	530.3	530.3	530.6	530.6
	intensity %	52.5	47.2	51.0	52.9	54.2
O2	Position	531.5	531.2	531.2	531.2	531.5
	intensity %	5.7	9.7	9.7	7.3	7.9
O3	Position	532.3	532.4	532.3	531.9	532.4
	intensity %	2.7	4.1	3.6	5.9	4.0
Ti (Ti^{4+})	Position	459.3	459.1	459.1	459.3	459.3
	intensity %	19.6	19.8	20.7	21.5	21.0
Ti (Ti^{3+}) after sputtering	Position	457.5	457.4	457.4	457.6	457.7
	intensity %	1.6	2.2	2.3	2.7	3.2
Ru	Position	281.4	281.1	281.1	281.5	281.5
	intensity %	0.23	0.22	0.18	0.15	0.12
N_{pyd}	Position	400.5	400.3	400.3	400.6	400.7
	intensity %	1.4	1.6	1.2	0.9	1.0
N_{NCS}	Position	398.4	398.1	398.1	398.3	398.2
	intensity %	0.6	0.7	0.5	0.3	0.3
N_{TBA}	Position	402.6	402.2	401.9	-0.2	-0.2
	intensity %	0.3	0.2	0.1	0.0	0.0
S1	Position	162.3	162.0	162.1	162.4	162.4
	intensity %	0.3	0.3	0.3	0.1	0.1
S2	Position	163.1	162.6	163.0	163.0	163.0
	intensity %	0.2	0.2	0.1	0.2	0.1

UPS- MIES results:

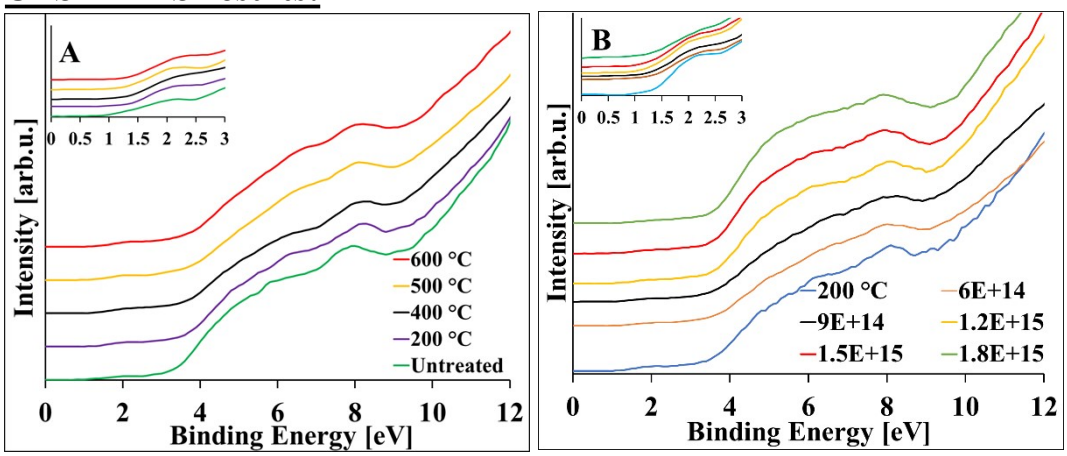

Figure S 6: UP spectra after dye adsorption for (A) pre-heated, (B) pre-heated/sputtered TiO_2 surfaces. The inset shows the UP spectra at low binding energies.

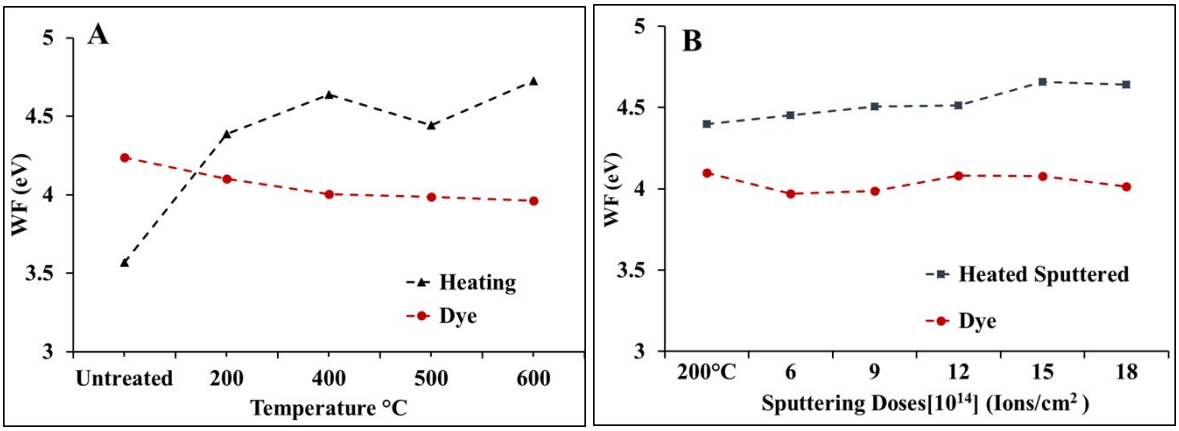

Figure S 7: The work function of A) pre-heated and B) pre-heated/sputtered TiO_2 samples before and after dye adsorption.

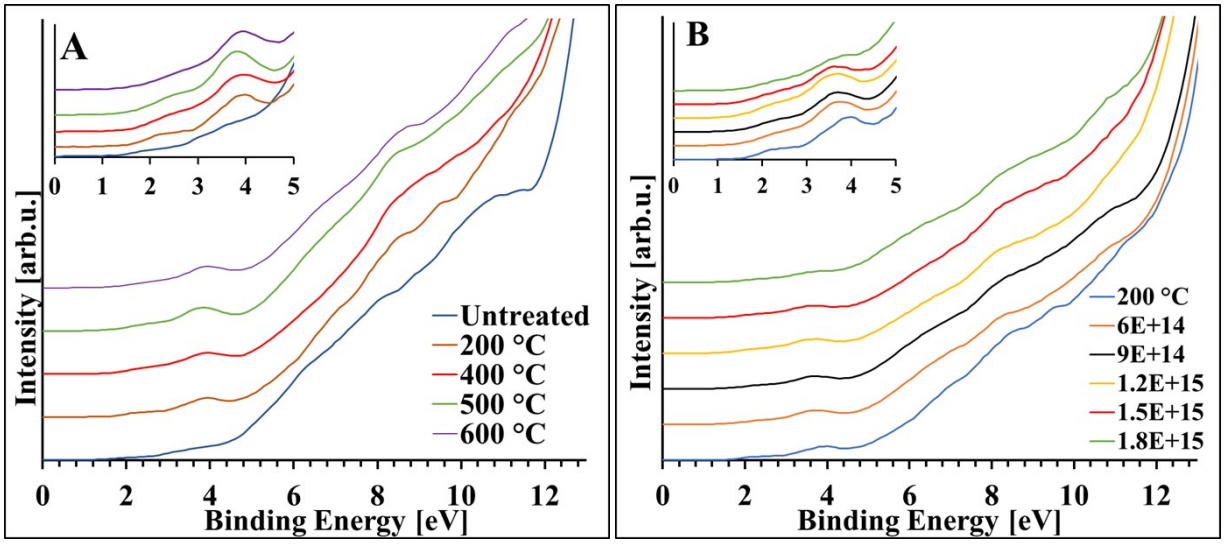

Figure S 8: MIE spectra after dye adsorption for (A) pre-heated, (B) pre-heated/sputtered TiO_2 surfaces. The inset shows the MIE spectra in the low binding energy region.

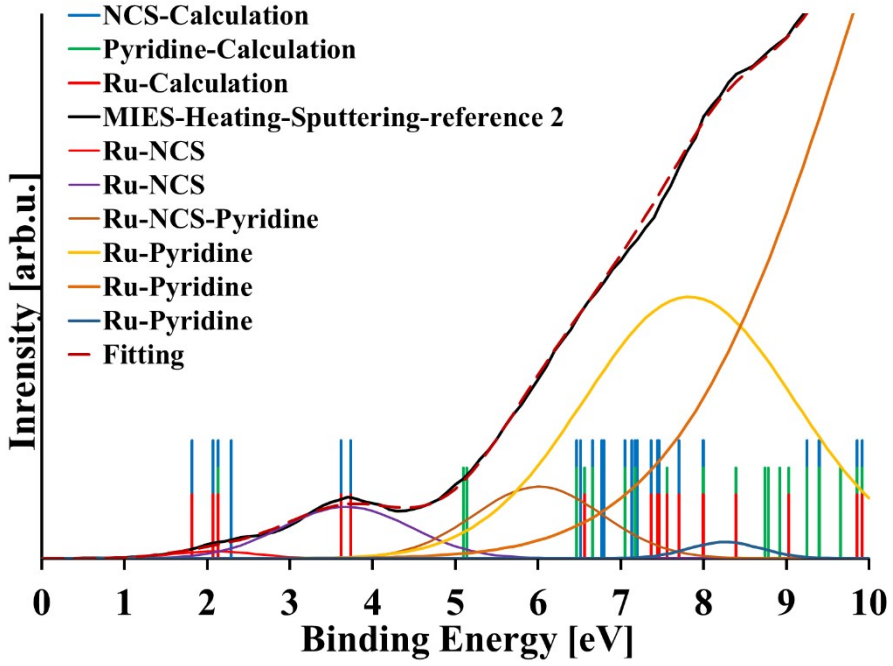

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Figure S 9: Gaussian peak model of the MIE Reference spectrum-2 of the pre-heated/sputtered TiO_2 samples. The calculated energy levels from the DFT calculations are shown as vertical lines.

AFM results

Figure S 10 to S 13 show the AFM images of the samples listed in Table 1. The red squares represent the areas where roughness was determined. The area of each red square was 10x10 nm and for each sample approximately 30 of these regions were analysed, with the values reported in Table 1 being an average and the error 1 standard deviation in each data set. Given that each image has a pixel density of 512x512 then we calculate there is ~ 26x26 data points in each 10x10 nm red square. The roughness values represent the average roughness, R_a, and the R_q (RMS). R_a and R_q roughness are standard analysis methods to report surface roughness using AFM. They differ in their mathematical description of roughness. Where R_q is the root mean square average of the height deviations taken from the mean image data line and R_a is the arithmetic average of the absolute values of the surface height deviations measured from the mean plane. In many instances they give different answers but do often follow the same trends between images as we observed in our case

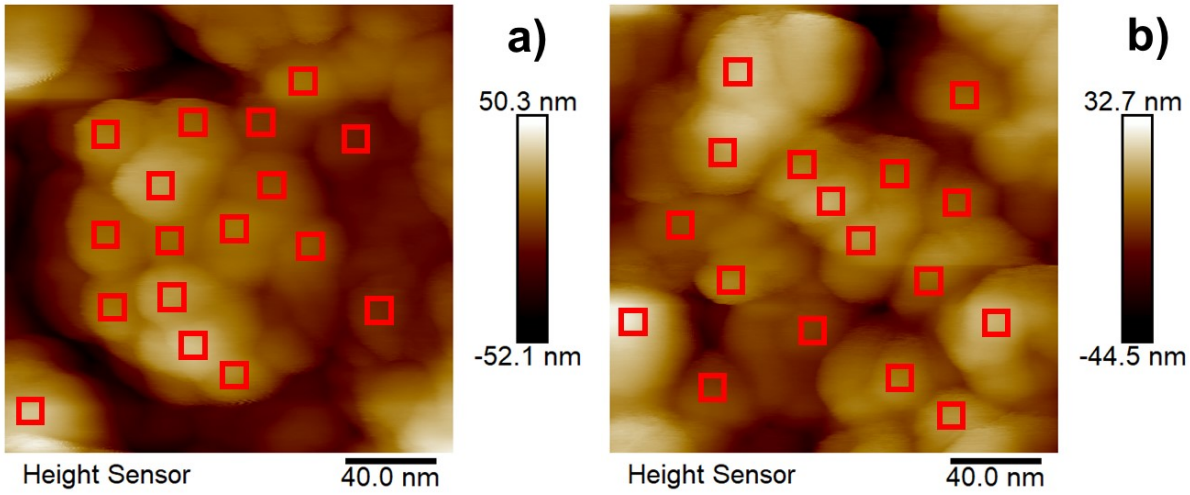

Figure S 10: a) and b) AFM images of the TiO_2 sample surfaces after heating to 200 C in UHV and no sputtering. , b) heating to 200 C in UHV and Ar^+ sputtering with a dose of $18x10^{14}$ ions/cm^2, c) no heating and d) heating in UHV to 500 C.

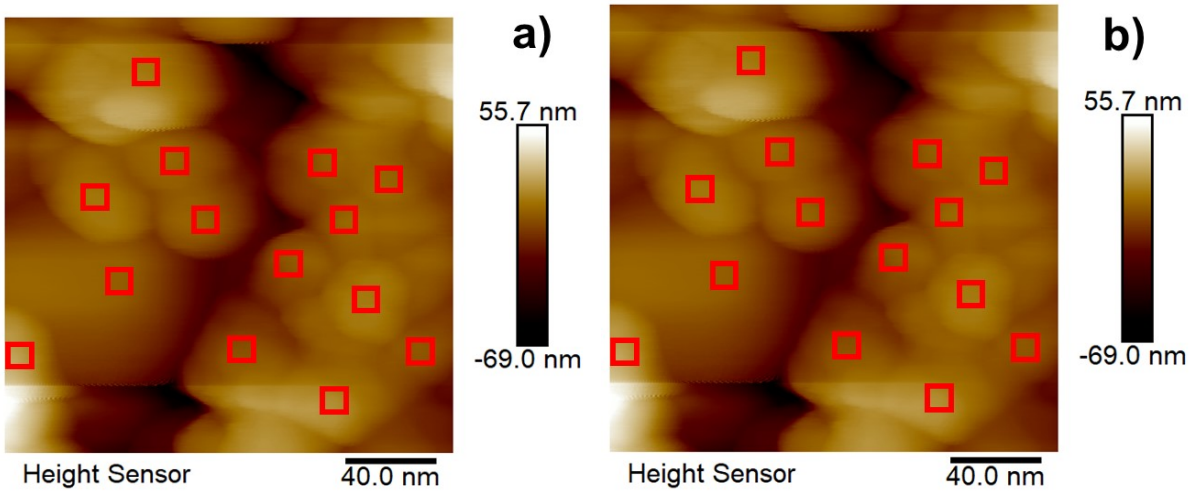

Figure S 11: a) and b) AFM images of the TiO_2 sample surfaces after heating to 200 C in UHV and Ar^+ sputtering with a dose of $18x10^{14}$ ions/cm^2.

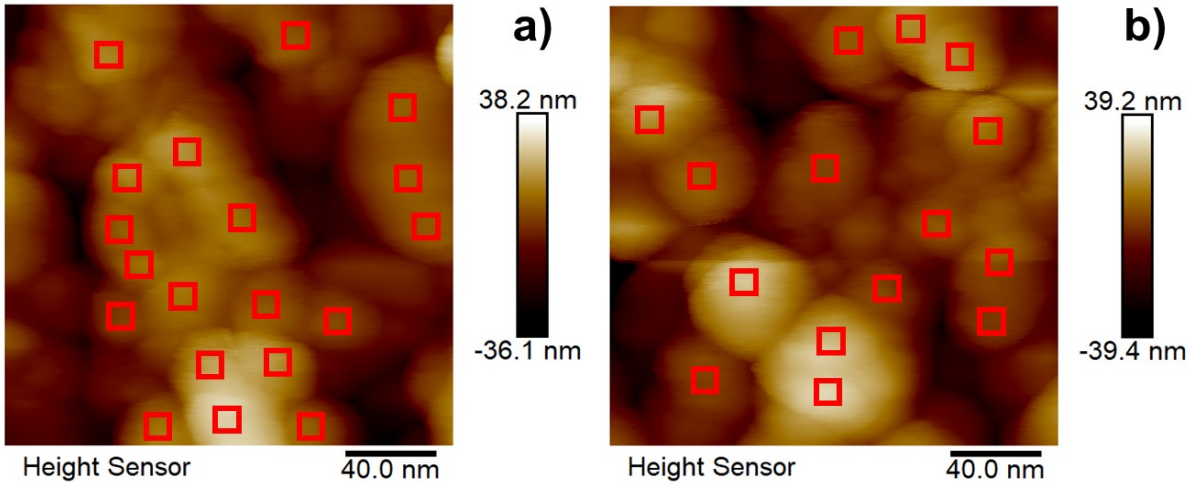

Figure S 12: a) and b) AFM images of the TiO_2 sample surfaces without heating.

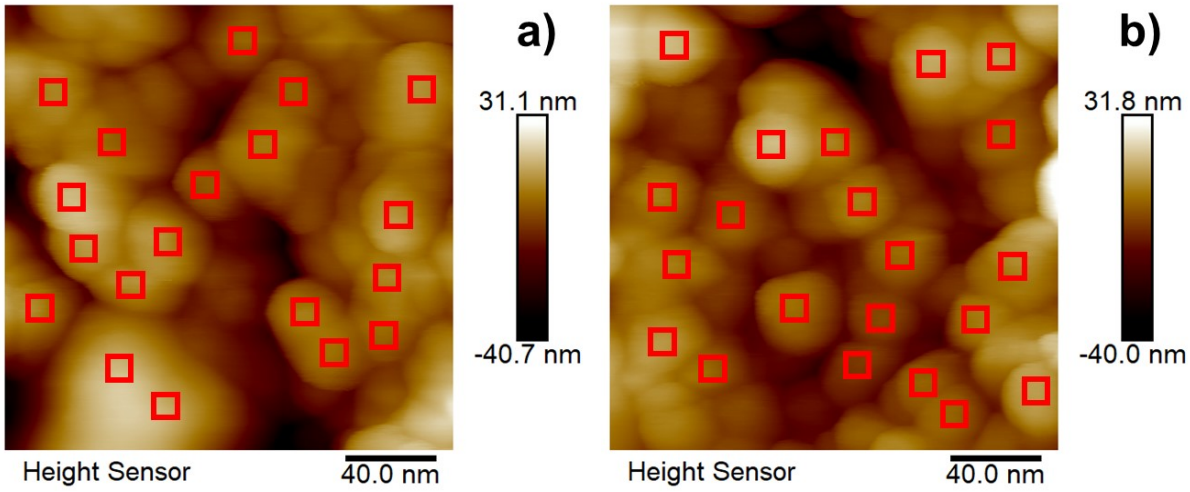

Figure S 13: a) and b) AFM images of the TiO_2 sample surfaces after heating in UHV to 500 C.