

At the interface between organic radicals and TiO₂(110) single crystals: electronic structure and paramagnetic character

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Electronic Supporting Information

This Electronic Supplementary Information provides

- 1) Experimental details.
- 2) Tables 1-3 with all fit parameters for XPS C1s core level spectra.
- 3) Tables 4-6 with all fit parameters for XPS N1s core level spectra.
- 4) The XPS spectra after film annealing at 790 K.
- 5) The XPS Ti2p core level of two surfaces with different densities of Ti³⁺ 3d states and the relative tables with all fit parameters.
- 6) Relevant pK_a/pH values in solution.

Further experimental details.

Sample preparation and XPS investigations were performed both in our laboratory and at the BESSY II synchrotron source (Berlin, Germany) at the UE52-PGM-PES.

Our system consists of a preparation chamber, and an analysis chamber (base pressure = 1×10^{-10} mbar) equipped with a concentric hemispherical Specs Phoibos 150 analyser and a monochromatized Al K α X-ray source.

The measuring chamber (base pressure = 4×10^{-10} mbar) at the UE52-PGM-PES undulator beamline is equipped with a standard twin anode X-ray source, and a SCIENTA R4000 electron energy analyzer. The measurements were carried out in low-alpha and single bunch (ring current at injection = 13/20 mA (mode B/mode A), cff = 2.5, analyser resolution = 0.1 eV). We found that these operation modes minimise the radiation damage. The C1s photoelectron spectra at BESSY were taken with 1000 eV photon energy. As the substrate already contains oxygen, we concentrate only on carbon and nitrogen species.

Clean TiO₂(110) single crystals were prepared using multiple cycles of argon ion sputtering and UHV annealing.¹ The surface preparation was monitored by XPS and X-ray absorption spectroscopy. The change in colour of the crystals from transparent to light blue/gray indicated the oxygen deficient surface. The molecules were deposited by OMBD under UHV conditions keeping the substrate at room temperature (evaporation rate = 1 Å /min, determined with a quartz microbalance).

No degradation of the samples was observed on the time scale of all presented experiments.

1. F. Allegretti, S. O'Brien, M. Polcik, D. I. Sayago and D. P. Woodruff, *Phys. Rev. Lett.*, 2005, **95**, 226104.

Table 1: NitPyn fit results for energy position and relative areas of the photoemission lines in the C1s spectra for a 0.3 nm nominally thick film:

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	284.04	0.08	1.32	31.45
C-H	284.32	0.08	1.32	38.94
CH₃	284.60	0.08	1.32	17.13
C-N	286.27	0.08	1.32	9.98

Table 2: NitPyn fit results for energy position and relative areas of the photoemission lines in the C1s spectra for a 0.5 nm nominally thick film.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	284.02	0.08	1.32	31.30
C-H	284.30	0.08	1.32	39.10
CH₃	284.58	0.08	1.32	17.20
C-N	286.01	0.08	1.68	12.40

Table 3: NitPyn fit results for energy position and relative areas of the photoemission lines in the C1s spectra for a 1.0 nm nominally thick film.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
C-C	284.02	0.08	1.32	31.20
C-H	284.30	0.08	1.32	36.50
CH₃	284.58	0.08	1.32	16.45
C-N	286.01	0.08	1.68	14.21

Table 4: NitPyn fit results for energy position and relative areas of the photoemission and satellite lines in the N1s spectra for a 0.3 nm nominally thick film:

(~ 17% of Ti³⁺ 3d states)

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
Decomposed radical (N-H)	400.03	0.1	2.35	83.37
Ti -N	397.75	0.1	1.33	13.47
Satellite	402.93	0.1	2.03	3.16

(~ 3% of Ti³⁺ 3d states)

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
Intact radical	402.04	0.1	1.72	47.02
Decomposed radical (N-H)	399.76	0.1	1.72	33.73
Ti-N	398.14	0.1	1.72	11.63
Satellite	403.44	0.1	1.72	7.62

Table 5: NitPyn fit results for energy position and relative areas of the photoemission and satellite lines in the N1s spectra for a 0.5 nm nominally thick film:

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
Intact radical	401.92	0.1	1.32	47.58
Decomposed radical (N-H)	400.03	0.1	2.35	33.40
Ti-N	398.02	0.1	1.32	10.60
Satellite	403.32	0.1	1.32	4.48
Satellite	405.15	0.1	1.32	3.88

Table 6: NitPyn fit results for energy position and relative areas of the photoemission and satellite lines in the N1s spectra for a 1.0 nm nominally thick film:

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
Intact radical	401.92	0.1	1.32	56.14
Decomposed radical (N-H)	400.03	0.1	1.98	28.58
Ti-N	398.02	0.1	1.32	5.86
Satellite	403.32	0.1	1.32	9.41

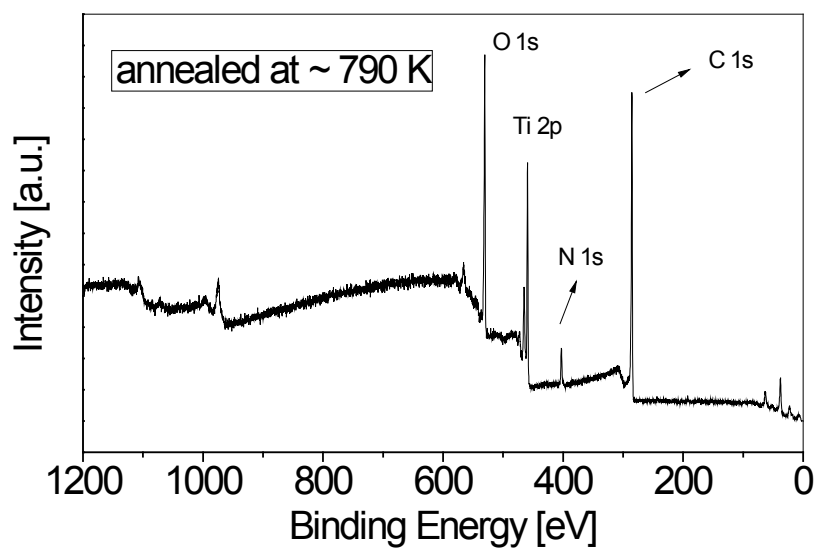
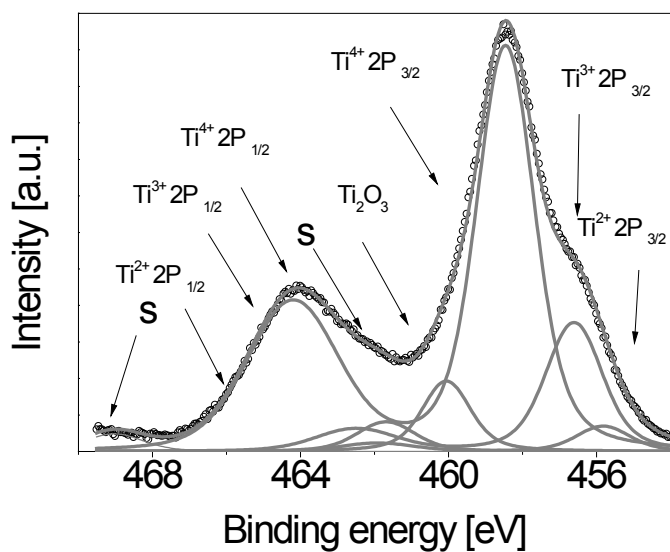
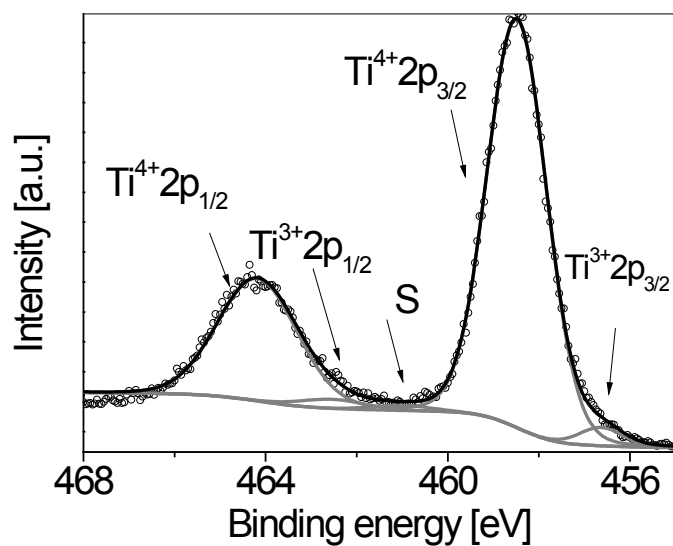


Figure 1S: XPS survey spectra after annealing @ 790 K of a 2 nm nominally thick NitPyn film.



	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
Ti⁴⁺(2p_{3/2})	458.50	0.70	1.45	44.71
Ti⁴⁺(2p_{1/2})	464.20	0.70	2.52	23.18
Ti³⁺(2p_{3/2})	456.60	0.70	1.41	14.29
Ti³⁺(2p_{1/2})	462.50	0.70	1.66	3.05
Ti²⁺(2p_{3/2})	455.83	0.70	1.35	2.46
Ti²⁺(2p_{1/2})	461.93	0.70	1.22	1.08
Ti₂O₃	460.05	0.70	1.13	6.30
Satellite	461.68	0.70	1.45	2.73
Satellite	468.68	0.70	1.45	2.18

Figure 2S: Ti2p core level spectra of the surface before deposition of a 0.3 nm thick film as in Figure 2a, together with the Table containing the fitting parameters.



	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)
$\text{Ti}^{4+}(2p_{3/2})$	458.50	0.70	1.48	68.17
$\text{Ti}^{4+}(2p_{1/2})$	464.20	0.70	2.00	27.11
$\text{Ti}^{3+}(2p_{3/2})$	456.65	0.70	1.06	2.25
$\text{Ti}^{3+}(2p_{1/2})$	462.55	0.70	1.60	1.63
Satellite 1	461.02	0.70	1.48	0.84

Figure 3S: Ti2p core level spectra of the surface before deposition of a 0.3 nm thick film as in Figure 2b, together with the Table containing the fitting parameters.

Relevant pK_a/pH values in solution from Ref. 25.

The nitronyl nitroxide radical derivatives in benzene with triphenylphosphine spontaneously lose an oxygen atom. The compounds are weak bases and they may be reversibly protonated without decomposition. The compound with substituent = C_6H_5 has a $pK_a=1.9$.

The unsubstituted derivative with substituent =H undergoes deuterium exchange at the central carbon atom at pH 7, within 6 hours.

The formation of a compound as in Figure 4S occurs, after decomposition without degradation, when the solid with substituent =H, is kept at room temperature.

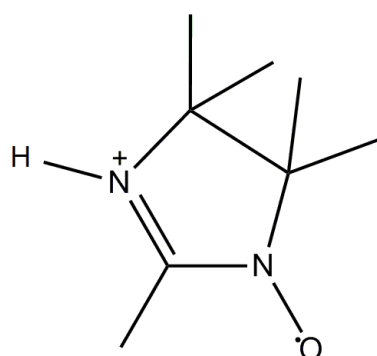


Figure 4S: One of the possible derivatives of the nitronyl nitroxide radical as from Ref. 25.