

Electronic Supplementary Information (ESI)

The Role of Mn Doping and Ti^{3+} Defects at TiO_2 Surfaces Reacting with NO and SO_2 Gases Investigated Using Near-Ambient Pressure X-ray Photoelectron Spectroscopy

Jack Chun-Ren Ke,^{ab} Andrew Thomas,^{ab*} Joseph Peake,^c and Robert Sayer^c

a. Department of Materials, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

b. Photon Science Institute and Henry Royce Institute, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

c. Croda Europe Ltd., Cheshire WA8 8UB, UK

Corresponding authors (emails)

Dr A.G. Thomas: andrew.g.thomas@manchester.ac.uk

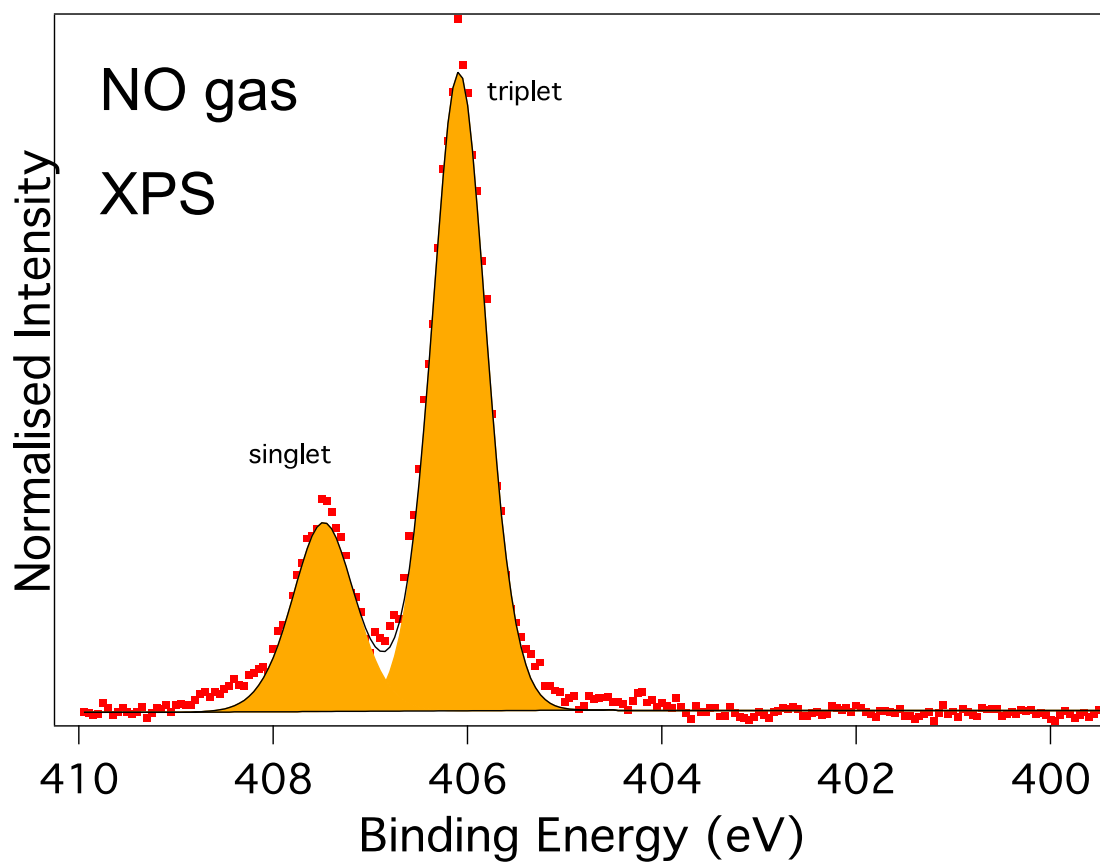


Figure S1 N 1s XPS spectrum of NO gas molecules during exposure to 1 mbar NO gas with the substrate was retracted from the analysis region. The two peaks arise from triplet/singlet splitting due to the paramagnetic electronic structure of NO.

	Sample	s-TiO ₂	r-TiO ₂	Mn-doped s-TiO ₂	Mn-doped r-TiO ₂
<i>During</i>	NO ₃ ⁻	0.03±0.01	0.08±0.02	0.06±0.02	0.16±0.02
	NO ₂ ⁻	N.D.*	N.D.	N.D.	0.25±0.05
	Total N	0.03±0.01	0.08±0.02	0.06±0.02	0.41±0.05
<i>After 1 hour</i>	NO ₃ ⁻	0.04±0.01	0.06±0.01	0.06±0.01	0.23±0.05
	NO ₂ ⁻	N.D.	N.D.	N.D.	0.12±0.02
	Total N	0.04±0.01	0.06±0.01	0.06±0.01	0.35±0.05
<i>After 2 hours</i>	NO ₃ ⁻	0.04±0.01	0.06±0.01	0.06±0.01	0.26±0.05
	NO ₂ ⁻	N.D.	N.D.	N.D.	0.07±0.01
	Total N	0.04±0.01	0.06±0.01	0.06±0.01	0.33±0.05

Table S1: N-components at the single crystal surface for the various surface treatments following exposure to NO gas and after 1 and 2 hours. *N.D. = not detected.

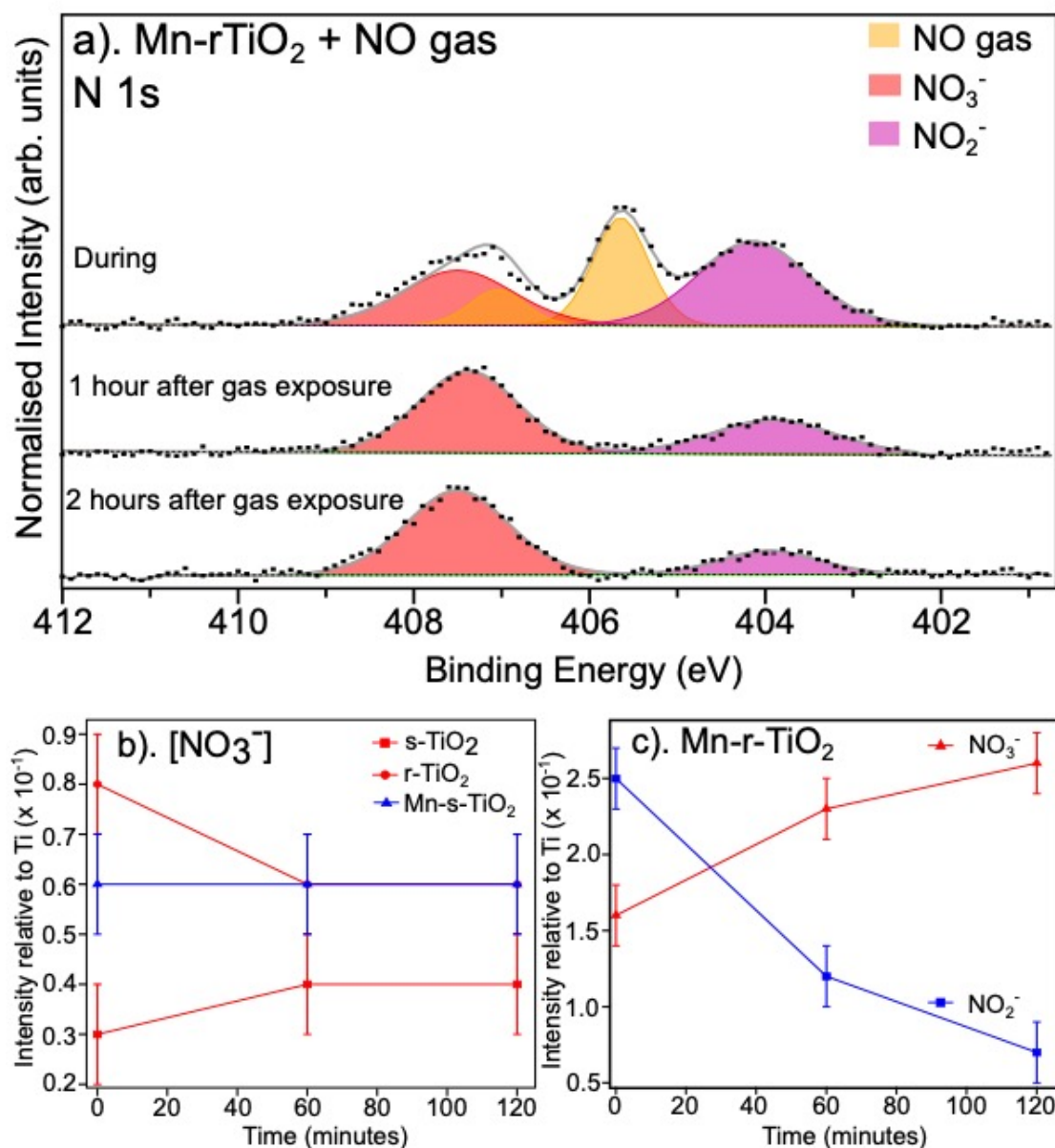


Figure S2 a) N 1s NAP-XPS spectra of the Mn-doped defective rutile (110) single crystal during and 1 hour and 2 hours after exposure to 1 mbar to show the evolution of the NO-conversion by-products. b) NO₃⁻ concentration for the stoichiometric (s-TiO₂), reduced (r-TiO₂) and Mn-doped stoichiometric single crystals over time showing little change over time and c) NO₃⁻ and NO₂⁻ concentrations on the Mn-doped reduced TiO₂ (Mn-r-TiO₂) with time. It appears NO₂⁻ is converted to NO₃⁻ over time, although there is also a slight decrease in the overall N-concentration at the surface over time.

	Sample	r-TiO ₂	Mn-doped s-TiO ₂	Mn-doped r-TiO ₂ *
<i>Before exposure to SO₂</i>	Ti ³⁺	31.3±5	5.5±1	66.7±5
	Ti ⁴⁺	68.7±5	94.5±1	33.3±5
<i>During</i>	Ti ³⁺	36.2±5	2.8±1	55.3±5
	Ti ⁴⁺	<u>63.8±5</u>	<u>97.2±1</u>	<u>44.7±5</u>
<i>After</i>	Ti ³⁺	<u>35.3±5</u>	<u>2.9±1</u>	<u>52.2±5</u>
	Ti ⁴⁺	<u>64.7±5</u>	<u>97.1±1</u>	<u>47.8±5</u>

Table S2. Ti³⁺:Ti⁴⁺ ratios for the various surface treatments during and after exposure to a SO₂/Ar gas mixture. *Note that the Mn-doped r-TiO₂ sample was heavily reduced and that the Ti³⁺ component is likely also to contain some other low oxidation states of Ti (i.e. Ti²⁺)

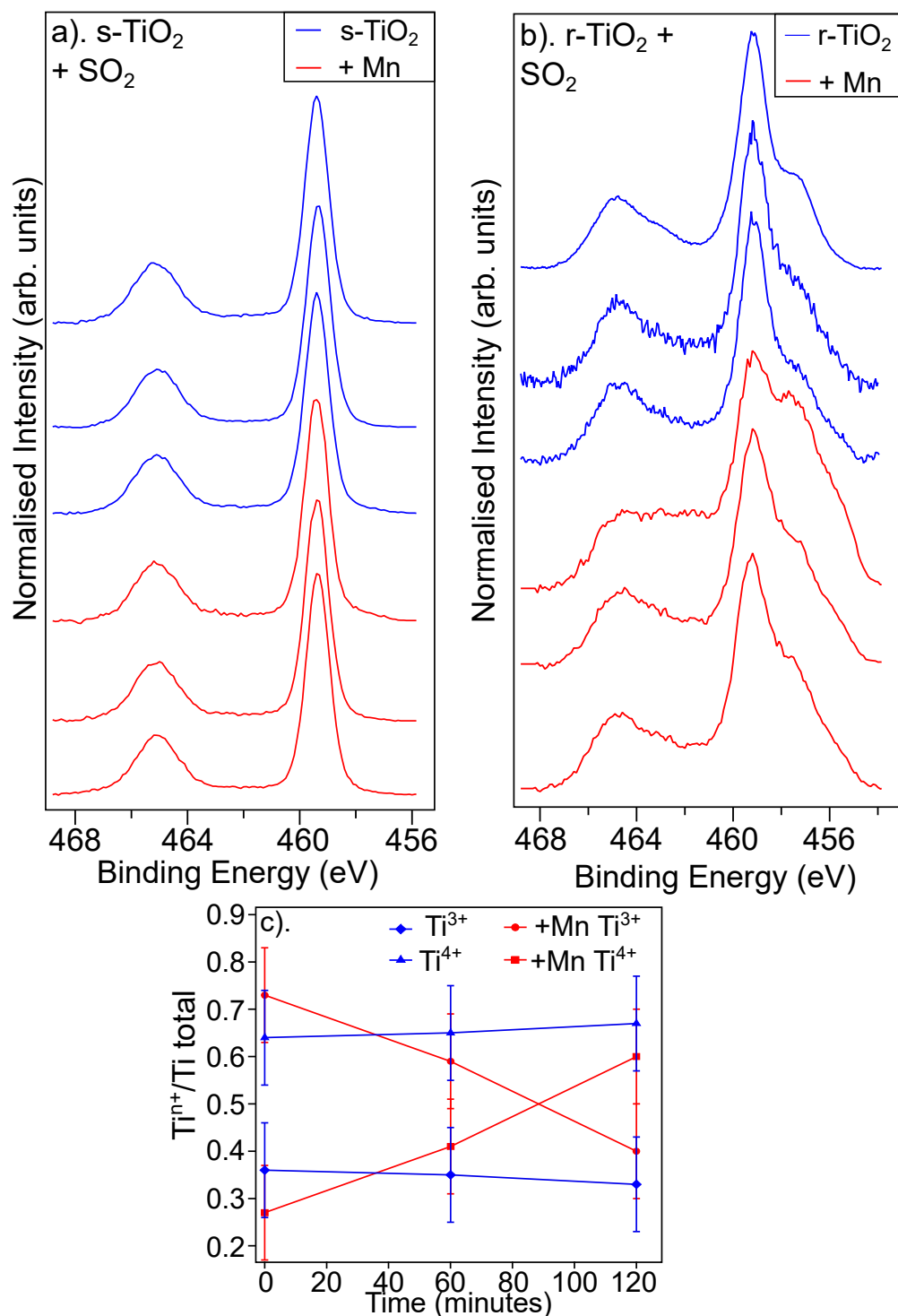


Figure S3. Ti 2p spectra recorded from a). stoichiometric TiO₂(110) with and without Mn doping before during and after exposure to SO₂ in Ar gas, and b) reduced TiO₂(110) with and without Mn doping before during and after exposure to SO₂ in Ar gas. c). shows the variation in Ti^{3+} and Ti^{4+} peak areas for the two reduced surfaces from b) indicating that there is only minimal change in Ti^{3+} removal in the reduced surface but that the Mn-doped surface leads to reoxidation of the TiO₂ surface by the SO₂/Ar gas mixture.

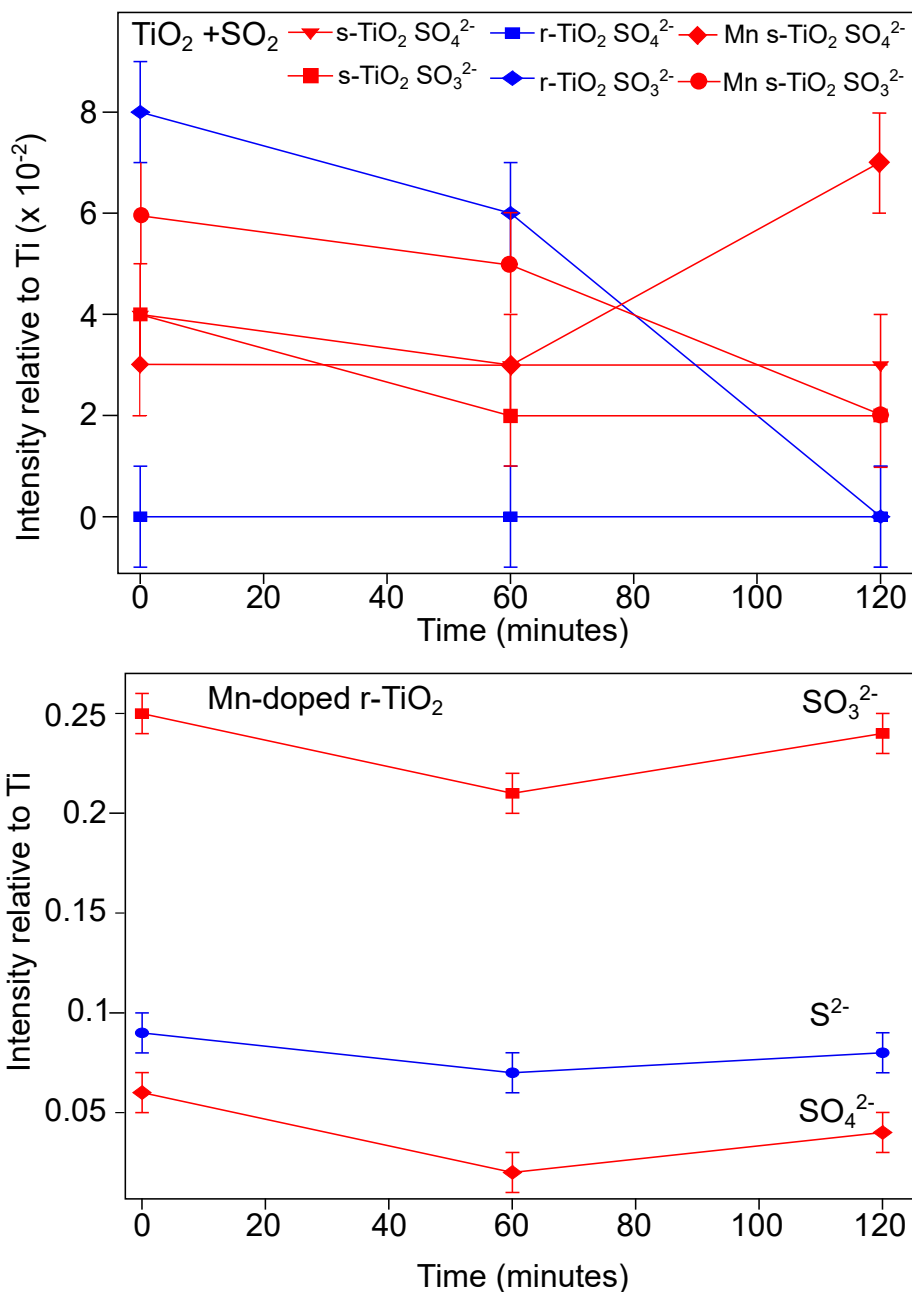


Figure S4. The top panel shows the amount of SO_3^{2-} and SO_4^{2-} species found on stoichiometric (s-TiO₂) and reduced (r-TiO₂) single crystal TiO₂(110) surfaces, along with the Mn-doped stoichiometric TiO₂ surface (Mn s-TiO₂) relative to the Ti 2p_{3/2} peak area. The lower panel shows the sulphur species for the Mn-doped reduced surface, where an additional feature for sulphide species is observed. The sulphide content remains constant and is accompanied by a decrease in Ti^{3+} as shown in Figure S3.

	Sample	s-TiO ₂	r-TiO ₂	Mn-doped s-TiO ₂	Mn-doped r-TiO ₂
<i>During</i>	SO ₄ ²⁻	0.04±0.01	N.D.	0.03±0.01	0.06±0.02
	SO ₃ ²⁻	0.04±0.01	0.08±0.02	0.06±0.01	0.25±0.05
	S ²⁻	N.D.*	N.D.	N.D.	0.09±0.01
	Total S	0.08±0.02	0.08±0.02	0.09±0.02	0.40±0.05
<i>After 1 hour</i>	SO ₄ ²⁻	0.03±0.01	N.D.	0.03±0.01	0.02±0.05
	SO ₃ ²⁻	0.02±0.01	0.06±0.01	0.05±0.01	0.21±0.02
	S ²⁻	N.D.	N.D.	N.D.	0.07±0.01
	Total S	0.05±0.02	0.06±0.01	0.08±0.02	0.30±0.05
<i>After 2 hours</i>	SO ₄ ²⁻	0.03±0.01	N.D.	0.07±0.01	0.04±0.01
	SO ₃ ²⁻	0.02±0.01	0.05±0.01	0.02±0.01	0.24±0.05
	S ²⁻	N.D.	N.D.	N.D.	0.08±0.01
	Total S	0.05±0.02	0.05±0.01	0.09±0.01	0.36±0.05

Table S3: S-components at the single crystal surface for the various surface treatments following exposure to SO₂ in Ar gas and after 1 and 2 hours. *N.D. = not detected.

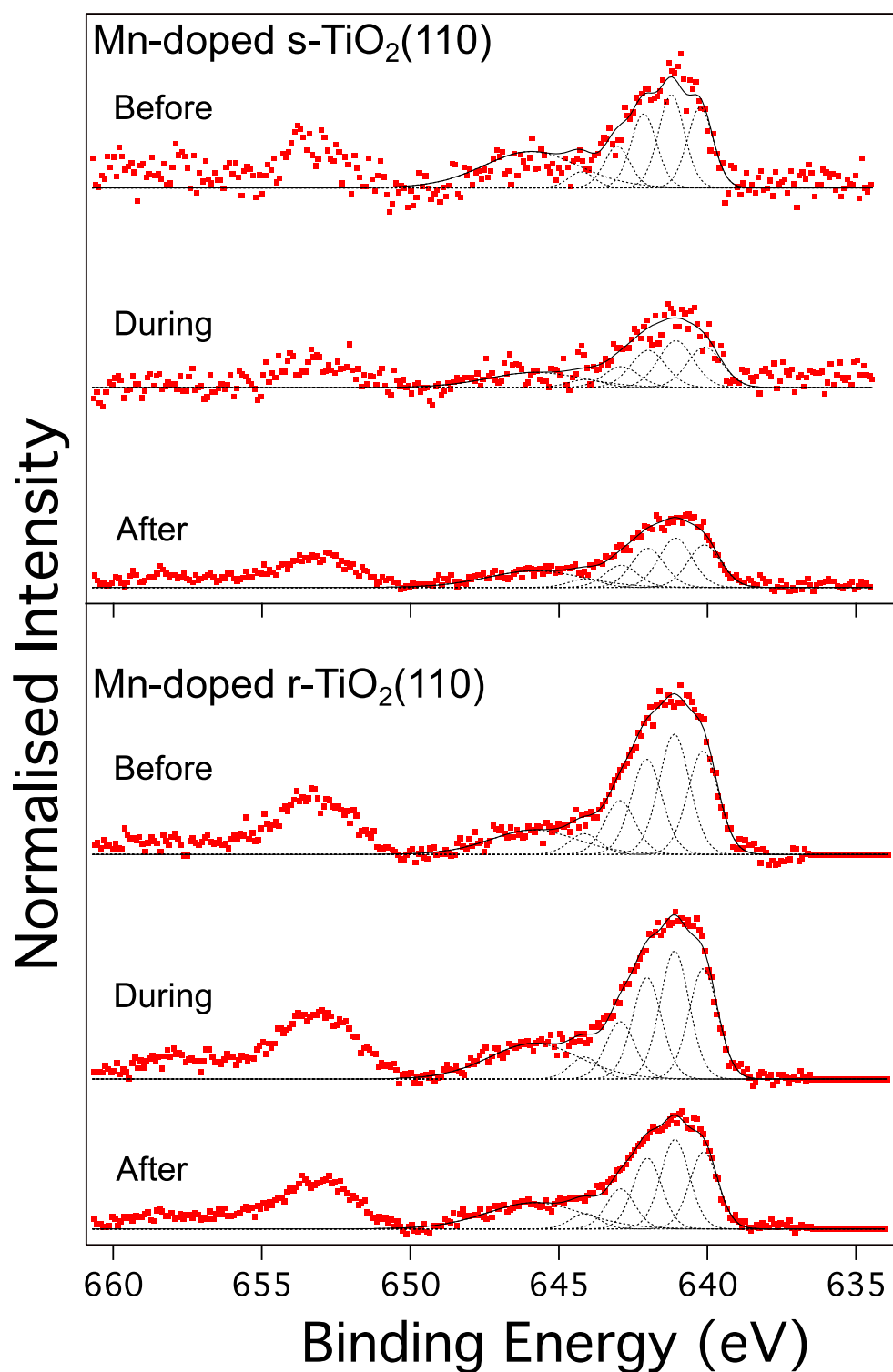


Figure S5. Mn 2p spectra following deposition of Mn on stoichiometric TiO₂(110) (top) and reduced TiO₂(110) (bottom panel). Spectra are shown fitted with multiplet fitting for MnO (Mn²⁺)[1], before during and after exposure to SO₂ gas. No significant changes are observed in the Mn 2p spectra. The spectra recorded from the r-TiO₂ sample have a better signal to noise ratio, associated with the higher uptake of Mn on this surface (see main manuscript).

O-species and binding energy(eV)	s-TiO ₂ (110)	r-TiO ₂ (110)	s-TiO ₂ (110) + Mn	r-TiO ₂ (110) + Mn	Croda 1 (Mn)	Croda 2
Oxide (530.6)	86.4	80.3	87.2	72.5	72.5	84.6
Ti-OH (531.7)	8.9	14.2	10.0	18.8	16.7	6.3
H₂O (532.7)	4.8	5.6	2.8	8.7	10.8	9.1

Table S4. Contributions of different O-species to the O 1s spectra for the different sample treatments and samples. Peak assignments are taken from Jackman *et al.* [2] Binding energies for the different O-contributions are given in parentheses.

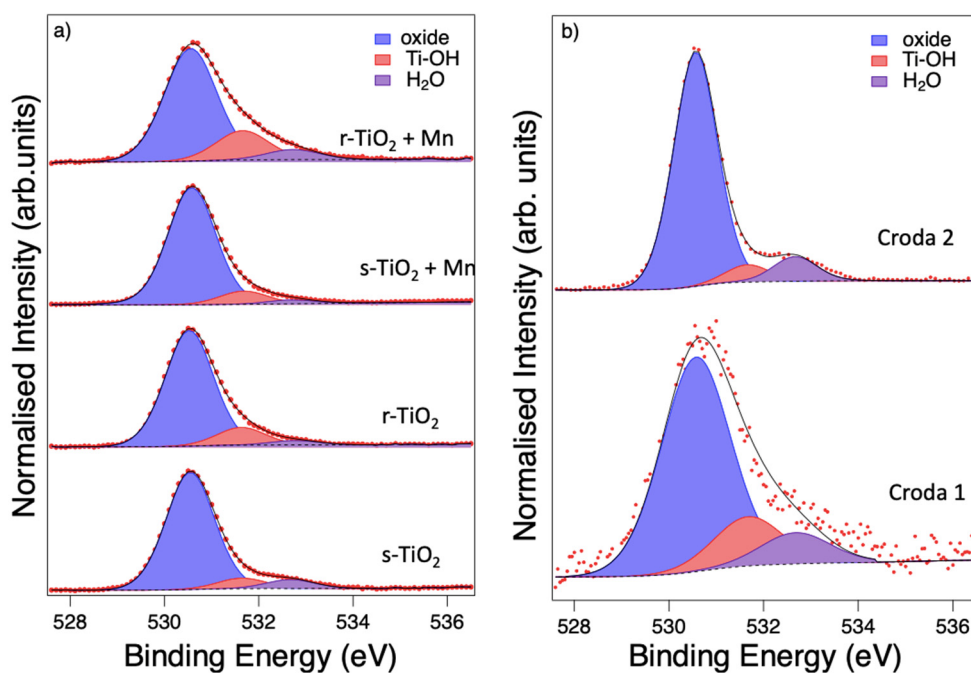


Figure S6. O 1s spectra recorded from a) single crystal samples s-TiO₂, r-TiO₂, s-TiO₂+Mn and r-TiO₂+Mn and b) Croda 1 and Croda 2. Peak binding energies and assignments are in good agreement with those seen for water adsorption on anatase TiO₂ [2].

Sample	Total N	NO ₃ ⁻	NO _{ads}	Total S	SO ₄ ²⁻	SO _{2 ads}
Croda 1	0.47±0.07	0.27±0.05	0.2±0.05	0.07±0.02	0.05±0.01	0.07±0.01
Croda 1 + H ₂ O	0.65±0.08	0.35±0.07	0.30±0.04	-	-	-
Croda 2	0.28±0.07	0.17±0.05	0.11±0.05	0.07±0.01	0.07±0.01	N.D.
Croda 2 + H ₂ O	0.21±0.04	N.D.	0.21±0.04	-	-	-

Table S5: N and S concentrations on the two TiO₂ nanopowders two hours after exposure to NO or SO₂/Ar gas. Note that the effect of water on SO₂ adsorption was not measured.

Calculation of Mn overlayer thickness.

Without STM measurements the nature of the Mn growth is not easy to determine. An estimate of the overlayer thickness can, however, be made assuming a continuous, uniform film of Mn on top of the TiO₂ substrate, using a two-layer model using the equation below[3];

$$\frac{I_{Mn2p}}{I_{Ti2p}} = \frac{N_{Mn}}{N_{Ti}} \frac{1 - \exp\{-\frac{d_{Mn}}{\lambda_{Mn}(E_{Mn})\cos\theta}\}}{\exp\{-\frac{d_{Mn}}{\lambda_{Mn}(E_{Ti})\cos\theta}\}},$$

where d_{Mn} is the thickness of the Mn overlayer, $\lambda_{Mn}(E_{Mn})$ is the inelastic mean-free path (IMFP) of Mn 2p electrons through the Mn overlayer at the kinetic energy of the Mn 2p photoelectrons = 1.5 nm. $\lambda_{Mn}(E_{Ti})$ is the IMFP of Ti 2p electrons through the Mn overlayer at the energy of the Ti 2p photoelectrons = 1.7 nm, $N_{Mn} = 47/\text{nm}^3$, and $N_{Ti} = 32/\text{nm}^3$ are the number densities of Mn and Ti atoms in the overlayer and TiO₂ substrate, and I_{Mn2p} and I_{Ti2p} are the intensities of the Mn 2p and Ti 2p photoemission peaks, corrected for the photoionisation cross-sections, analyser transmission function and sampling depth at the relevant kinetic energies. Since all of the measurements were performed in a normal emission geometry $\theta=0$, so $\cos\theta = 1$. This gives Mn overlayer thicknesses of 0.2 nm for the s-TiO₂ and 0.4 nm for the r-TiO₂ single crystal.

References.

1. Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni. *Applied Surface Science*, **257** (2011), 2717–2730.
<https://doi.org/10.1016/j.apsusc.2010.10.051>.
2. Jackman, M.J., Thomas, A.G., Murny, C., Photoelectron Spectroscopy Study of Stoichiometric and Reduced Anatase TiO₂(101) Surfaces: The Effect of Subsurface Defects on Water Adsorption at Near-Ambient Pressures. *The Journal of Physical Chemistry C* 119, (2015), 13682–13690.
<https://doi.org/10.1021/acs.jpcc.5b02732>.
3. Briggs and Seah, *Practical Surface Analysis: Auger and Photoelectron Spectroscopy* 2nd Edition (1990), John Wiley and Sons, Chichester.