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Supplementary Information

Insights into the surface of mesoporous NiO and its interaction with oxygen and water

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1 Supplementary Methods

1.1 UV-Vis gas cell and IR gas cell



Figure 1: (left) UV-Vis gas cell with holder for NiO glassy films inside. (right) IR gas flow cell with CaF₂ windows where one of the windows has NiO deposited on the side that points inwards.

1.2 Conductivity measurements and gas cell

A glassy substrate was decorated with metallic Al strips with a distance of 6 mm, that were used as connections in the four-point probe measurement, onto which the mesoporous NiO_x was deposited. A home-made gas flow cell then allowed to flow gases through the setup while measuring conductivity (see Figure S2 for picture of setup).



Figure 2: (left) Al fingers on glassy substrates onto which the mesoporous NiO films were deposited for conductivity measurements. (right) Gas cell for conductivity measurements with the four connection cables to the Al fingers under the NiO film.

1.3 X-ray spectroscopy

1.3.1 Sample mounting



Figure 3: Sample mounting for X-ray spectroscopy with thermal couple to the metal sled and spot-welded metal connections to the sled that are connected to the FTO under the NiO film and on top of the NiO film.

1.3.2 XPS Intensity calibration

A variation of total intensity of time-resolved spectra at different ambient pressure is observed at in-situ APXPS measurement with gas injection (e.g. Figure 7a in main text) which is mainly due to the inelastic scattering of photoelectrons going through the gas phase to analyzer. And this is calibrated prior to curve-fitting by normalizing the intensity of spectra to their background region intensity where no features exist.

1.3.3 Curve fitting for O 1s

A linear background is used for O 1s spectra. The spectra energies for O 1s are used as is with no further calibration to observe the energy shift under temperature and gas ambient. Energy shifts of same values with O 1s were then applied to spectra at corresponding temperature. Igor pro is used for XPS spectra curve fitting. The energy spacing between different components in the O 1s spectrum is fixed and used for all O 1s spectra curve-fitting at different ambient and temperature conditions. The peak broadening is applied with a Voigt function to give a pseudo-convolution of Lorentzian and Gaussian function, in which the Lorentzian broadening is contributed from the finite life time of core-hole formed from ejection of photoelectron from core level, and Gaussian function is used to express the instrumental and experimental broadening. The total peak width (FWHM), giving the energy resolution of the spectrometer is thus defined as,

$$\Delta E = \sqrt{\Delta E_{lor}^2 + \Delta E_{gau}^2} \tag{1}$$

The variation of temperature gives thermal broadening of peak width which was considered in the curve fitting. And this can be determined by thermal dependence of Fermi-Dirac distribution of fermi edge.

$$f(E) = \frac{ln(\sqrt{2}+1)}{\gamma_f} \times \frac{1}{\cosh^2(2ln(\sqrt{2}+1)E/\gamma_f)}$$
(2)

The thermal broadening to the FWHM is thus given by

$$\gamma_f = 4\ln(\sqrt{2} + 1)k_B T \approx 7/2k_B T \tag{3}$$

AP-XPS measurement taken at 25 to 300 °C in this work contribute to the peak broadening of 90 to 170 meV.

1.3.4 Ni 2p analysis with bulk subtraction

In-situ Ni 2p spectra at different temperatures and time-resolved spectra during gas injection are analysed by subtracting the bulk NiO signal from HAXPES to investigate the surface species. The Ni 2P HAXPES is curve fitted based on previous experimental and theoretical studies (SI, Figure S19) after a normalization to the total intensity (peak area). The double peak feature at main peak is fitted with two components at 853.8, 855.6 eV, attributing to lattice NiO and its non-local screening effect, respectively. The three components fitted at higher energies of 861.0, 864.1, and 866.6 eV are assigned to the satellite feature. To apply the fitted NiO bulk signal to the Ni 2p spectra obtained with soft x ray in synchrotron radiation facility, a narrowing on corresponding peak width, specifically on Gaussian broadening portion is needed due to the difference in energy resolution between the two instruments and light source. The narrowing is applied on the mainline and non-screening effect (the two peaks at lowest binding energy). The width is adjusted by using the Ga source spectrum to curve-fit the synchrotron data to align its raw data shape. After fixing the shape of the bulk Ni 2p spectra, the subtraction by the bulk Ni 2p is applied on the spectra from in-situ and gas dosing APXPS with normalization to their total peak area. Offset of BEs are applied to each spectra to calibrate to lattice NiO peak position.

1.3.5 XPS peak deconvolution

Table 1: Fitting parameters for O 1s giving the binding energy (BE), the area, the Full-Width-Half-Maximum (FWHM) and L/G for each peak.

		RT	75°C	125°C	200°C	300°C
Peak 1	BE (eV)	529.4	529.5	529.5	530.1	530.3
	area	0.45	0.46	0.49	0.54	0.6
	FWHM	0.98	0.98	1	1.03	1.06
	L/G	0.13	0.13	0.13	0.16	0.15
Peak 2	BE (eV)	530.8	530.9	530.9	531.5	531.7
	area	0.17	0.1	0.05	0.05	0.05
	FWHM	1.08	1.08	1.1	1.12	1.14
	L/G	0.15	0.15	0.15	0.14	0.14
Peak 3	BE (eV)	531.4	531.4	531.4	532	532.3
	area	0.32	0.36	0.35	0.29	0.25
	FWHM	1.12	1.12	1.13	1.18	1.2
	L/G	0.14	0.14	0.14	0.14	0.13
Peak 4	BE (eV)	532	532	532.1	532.6	532.9
	area	0.03	0.06	0.1	0.12	0.09
	FWHM	1.18	1.18	1.2	1.22	1.24
	L/G	0.14	0.14	0.13	0.13	0.13
Peak 5	BE (eV)	532.9	533	533	533.6	533.8
	area	0.02	0.02	0.01	0	0
	FWHM	1.31	1.31	1.33	1.36	1.39
	L/G	0.17	0.17	0.16	0.16	0.16

2 Supplementary Figures and Discussion

2.1 Cyclic voltammetry of NiO_x film



Figure 4: CV of NiO_x film on glassy FTO substrate in glovebox.

2.2 Removal and reformation of surface states with inert gas flow



Figure 5: Absorption change with vacuum (100mbar) and Ar flow showing that vacuum can also remove some surface states, similarly to Ar gas flow.



Figure 6: Absorption change with the introduction of Ar gas that has been bubbled through water and adsorbs to a glass substrate, showing the diffraction of water.



Figure 7: Absorption change of heat-treated NiO_x on glassy substrates. The heat treatment was done on a hotplate in ambient atmosphere for 2 min. This shows that heat can also remove some surface states, similar to an inert gas flow.



Figure 8: Absorption of NiO_x films on FTO and the FTO slide itself. The absorption onset of the bandgap is around 400 nm.



Figure 9: (a) Absorption change and (b) kinetic traces of individual wavelength upon exposure to inert gas after initial bleach by heating to 200 °C for 2 min in air.



Figure 10: Kinetic traces of desorption/adsorption of water/oxygen mixture versus flow with pure oxygen.



Figure 11: Full absorption changes corresponding to the traces in the main text: (a) Ar/H_2O , (b) O_2/Ar .



Figure 12: (a) Bleach during Ar flow and (b) corresponding wavelength traces.



Figure 13: (a) IR absorption with the start of Ar flow of NiO_x on CaF_2 and (b) delta spectrum compared to 2min of Ar flow in IR region during Ar gas flow to better visualize the baseline drop.

2.3 Conductivity measurements

Since the surface states have been linked to conductivity in nickel oxide, and to further investigate the role of free carriers, we performed conductivity measurements during the flow of various gases. A steady flow of N_2 showed a significant decrease of conductivity of the NiO_x films that only marginally recovered upon subsequent exposure to oxygen (SI, Figure S14). While this is initially contradictory to the observations from FTIR spectroscopy, we also observed that a flow of oxygen yielded similar results and that the exposure to water with the help of a carrier gas instantly led to a drastic increase in conductivity (SI, Figure S14). This implies that four-point probe measurements for metal oxides in air have to the regarded with caution since physisorbed water results in a significant change in observed conductivity.



Figure 14: Four point-probe resistance measurements of NiO_x films on glass with Al fingers (a) upon N_2 flow and (b) oxygen flow afterwards. (c) Upon O_2 flow and then exposure to water by flowing N_2 through the gas cell that was bubbled through H_2O

2.4 Temperature and gas injection during ambient pressure X-ray photoelectron spectroscopy



Figure 15: (a) O1s spectra of NiO_x films with rising temperature that are normalised and shifted in binding energy (0.04, 0.07, 0.62 and 0.9 eV from 75 to 300 $^{\circ}$ C) so that the lattice oxygen peak is at same energy and (b) corresponding difference spectrum.



Figure 16: Ni2p XPS spectra of NiO_x films with rising temperature that are area normalised and shifted in binding energy and corresponding difference spectrum to room temperature (RT). The XPS at 450 $^{\circ}$ C also shows a clear metallic Ni feature.



Figure 17: Ni L normalized absorption spectra of NiO_x films with rising temperature. The film at 450 °C shows a reduction of nickel states to metallic Ni, as also seen in Ni2p XPS.



Figure 18: HAXPES spectra of NiO_x films (O1s, Ni2p and C1s) recorded with an Al source vs Ga source showing the bulk NiO spectrum (without surface species) with the Ga source compared to a more surface-sensitive Al source.



Figure 19: HAXPES Ni2p spectra fitted for data treatment in the main text figure 6.



Figure 20: O1s spectra of NiO_x films after heating/cooling procedure (a) before, (b) just after, and (c) during prolongued oxygen dosing.



Figure 21: Ni L normalized absorption spectra of NiO_x films during a sequence of heating to 200 °C and cooling to RT in vacuum followed by gas dosing and subsequent return to vacuum for (a) oxygen gas dosing and (b) water gas dosing.



Figure 22: O1s spectra of NiO_x films after heating/cooling procedure (a) before, (b) just after, and (c) during prolongued water dosing. The H₂O ratios in the spectra are 0%, 1%, and 7%, respectively.



Figure 23: O1s peak position of lattice oxygen during a sequence of heating to 200 °C and cooling to RT in vacuum followed by oxygen gas dosing and subsequent return to vacuum.



Figure 24. The C 1s under different temperatures. Surface impurities at 288 eV are shown and these mostly vanish after reaching 125 °C. Since peak 4 in O 1s increases with T and only start decreases at 300 °C, this clearly exclude a relation between peak 4 and the carbon impurities. Peak 2 shows an immediate decrease with T, and we cannot exclude that part of the intensity in peak 2 can be related to carbon impurities. However, its sensitivity to O_2 gas dosing reveals a high correlation to adsorbed oxygen.



Figure 25. a) The O 1s after a Shirley background subtraction. A slight asymmetric shape retains on O 1s, indicating the existence of surface species. b) The Intensity attenuation verses the depth relative to surface based on $I = I_0 e^{-\frac{d}{\lambda \sin \theta}}$, The IMFP of O 1s core level electron in

the depth relative to surface based on $I = I_0 e^{-\lambda \sin \theta}$. The IMFP of O Is core level electron in Ga source is estimated to be 11.6 nm (assuming NiO, TPP-2M, 6.67 g/cm³ density, 3.6 eV bandgap). The surface 1 nm will then take 9% of the total signal. The signal thus mainly exhibits the bulk feature.