Supporting Information (SI)

Facet-engineered TiO$_2$ nanomaterials reveal the role of water-oxide interactions in surface protonic conduction

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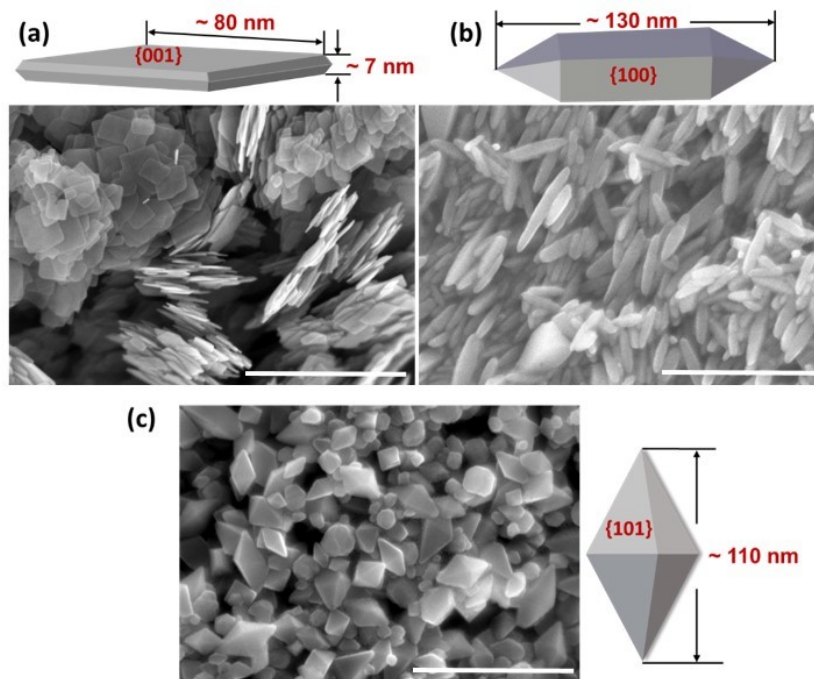[*]corresponding author: truls.norby@kjemi.uio.no

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Fig. S1: SEM images and indicative particle dimensions of (a) T001, (b) T100 and (c) T101. Scale bar is 500 nm.
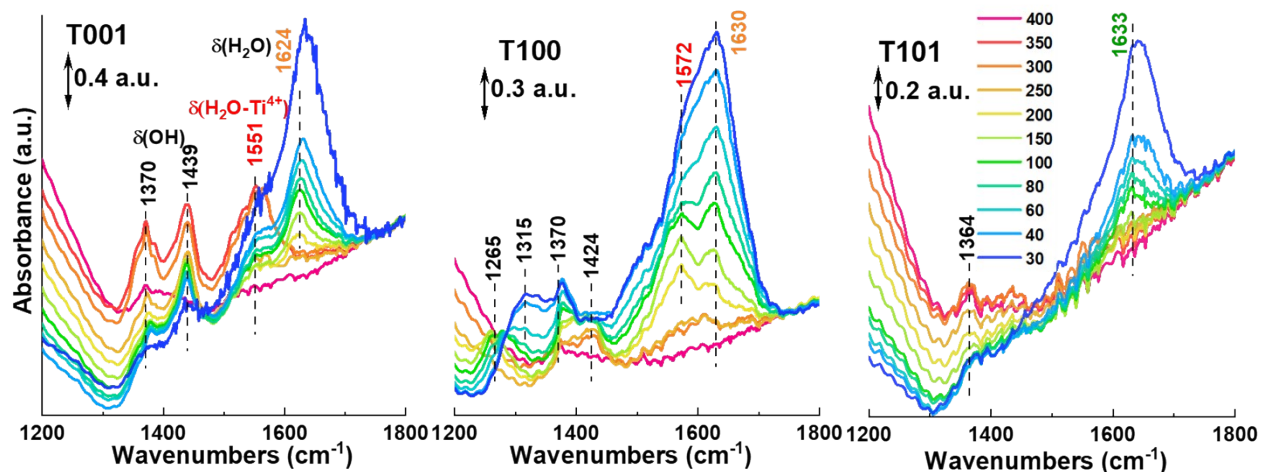

Fig. S2: FTIR spectra at low frequencies of TiO_2 samples for different temperatures (in °C) and progressive water vapor removal. The colors of the peak numbers correspond to the different temperatures.

Fig. S2 shows the FTIR spectra in the O-H bending region, two main peaks at around 1630 cm^{-1} and 1365 cm^{-1} are typical for the bending mode of physisorbed water molecules, $\delta(H_2O)$, and the

hydroxyls, $\delta(OH)$, respectively.[1] Using the 1630 cm^{-1} peak as an indicator, it can be safely concluded that most of the molecularly adsorbed water is removed at temperatures above 300 °C for both T100 and T001 samples. In the case of T101 this happens at 150 °C due to the weak hydrogen bonds among water molecules. A strong shoulder in the 1550-1600 cm^{-1} range of the T001 and T100 samples can be ascribed to the bending mode of H_2O molecules directly absorbed on the Ti^{4+} sites, which is still visible during the progressive outgassing process to 350 °C. In the $\delta(OH)$ vibration region, several new peaks (1265 and 1315 cm^{-1}) are observed in the T100 sample at temperatures below 100 °C, which might be related to the isolated hydroxyl groups.

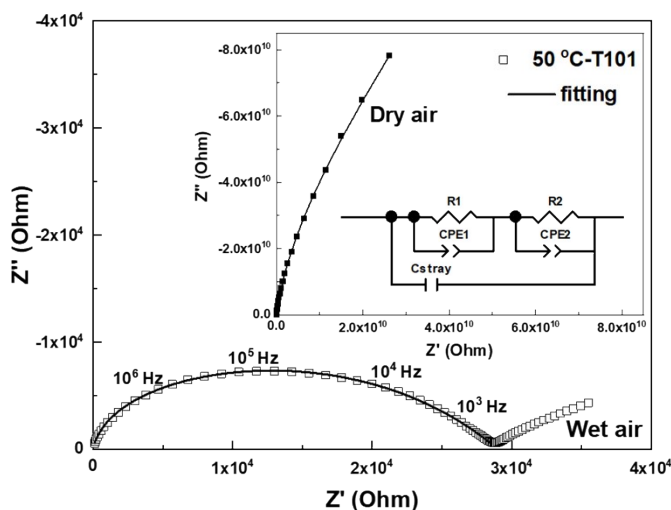**Fig. S3:** Nyquist plots of the T101 sample recorded in wet (p_{H2O} = 0.026 atm) and dry conditions at 50 °C, the inset shows also the equivalent circuit describing the proton transport and associated capacitances.

Fig. S3 shows Nyquist plots of impedance spectra for the T101 sample in wet and dry atmospheres at 50 °C. The response under wet conditions shows an arc at low frequencies attributed to the electrode impedance, and one arc at high frequencies with capacitances in the pF/cm range and attributed to surface protonic transport in the TiO_2. Many studies of surface protonics report two time constants in this range, suggested to reflect intra- and inter-grain surface protonic resistances [2]. In our results, this differentiation is not clear, and we only report the conductivity interpreted from a single arc. The result for dry conditions shows a partial arc of a much higher impedance, and no electrode impedance is visible.

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Table S1: Surface area and pore structure properties of TiO_2 samples

TiO_2	BET surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
T001	66.3	0.48	29.2
T100	50.5	0.56	44.2
T101	57.8	0.37	25.4

Table S2: Pre-exponentials and activation energies of total conductivities for porous TiO_2 samples with predominance of different surface facets, fitted with TableCurve2D to log(σT) vs 1/T plots. Data marked "H_2O", "D_2O", and "$0.5H_2O$" have $pH_2O = 0.026$ bar, $pD_2O = 0.023$ bar, and $pH_2O = 0.013$ bar, respectively. "Dry" means bottle-dry with pH_2O estimated at $3 \cdot 10^{-5}$ bar (30 ppm). Data for T100 and T001 in wet atmospheres were fitted to a model of the sum of bulk conductivity and surface protonic conductivity in chemisorbed and 1st solid physisorbed water layers. For T101, an additional intermediate surface protonic contribution is included. In "H_2O" and "D_2O" data an additional contribution from liquid-like physisorbed water was evident for the lowest temperature, which was therefore omitted in the fitting. In "$0.5H_2O$" data, this was not visible, and the lowest temperature point was included in the fitting. In dry atmospheres, only the bulk conductivity was fitted, and the lowest temperature points were omitted, to exclude surface protonic contribution. Parameters are given with standard deviations, in some cases with more digits than statistically appropriate, in order to have a consistent number of decimals and allow reproduction of the measured data.

		Bulk		Chemisorbed		Intermediate		1st (solid) physisorbed	
		Log (σ_0(SK/cm))	E_a(eV)	Log (σ_0(SK/cm))	E_a(eV)	Log (σ_0(SK/cm))	E_a(eV)	Log (σ_0(SK/cm))	E_a(eV)
T100	H_2O	5.67±2.13	1.30±0.29	-0.80±0.57	0.46±0.06			-14.55±0.15	-0.79±0.01
	D_2O	5.59±1.82	1.30±0.24	-1.12±0.80	0.47±0.08			-15.72±0.21	-0.86±0.02
	$0.5H_2O$	4.14±1.45	1.09±0.19	-1.20±0.85	0.46±0.08			-16.12±0.18	-0.84±0.01
	Dry	3.94±0.16	1.07±0.02						
T001	H_2O	5.84±0.27	1.24±0.04	-1.61±0.32	0.40±0.03			-14.23±0.06	-0.77±0.01
	D_2O	5.41±0.15	1.20±0.02	-3.08±0.29	0.28±0.03			-15.17±0.06	-0.819±0.004
	$0.5H_2O$	5.47±0.41	1.20±0.05	-2.91±0.72	0.32±0.07			-16.81±0.18	-0.87±0.01
	Dry	5.12±0.05	1.157±0.006						
T101	H_2O	8.78±3.59	1.59±0.47	0.40±0.45	0.49±0.05	-5.72±0.40	-0.08±0.03	-14.62±0.14	-0.71±0.07
	D_2O	5.45±0.63	1.14±0.09	-0.32±0.33	0.42±0.03	-6.50±0.46	-0.12±0.03	-15.65±0.12	-0.77±0.05
	$0.5H_2O$	5.59±1.95	1.17±0.28	0.70±0.96	0.54±0.10	-5.50±0.62	-0.03±0.05	-15.40±0.43	-0.72±0.03
	Dry	3.58±0.05	0.869±0.005						

References

1.   H. Lin, J. Long, Q. Gu, W. Zhang, R. Ruan, Z. Li and X. Wang, *Phys Chem Chem Phys*, 2012, **14**, 9468-9474.
2.   S. Ø. Stub, E. Vøllestad and T. Norby, *Journal of Materials Chemistry A*, 2018, **6**, 8265-8270.