Supporting Information for

Surface acidity of tin dioxide nanomaterials revealed with ^{31}P solid-state NMR spectroscopy and DFT calculations

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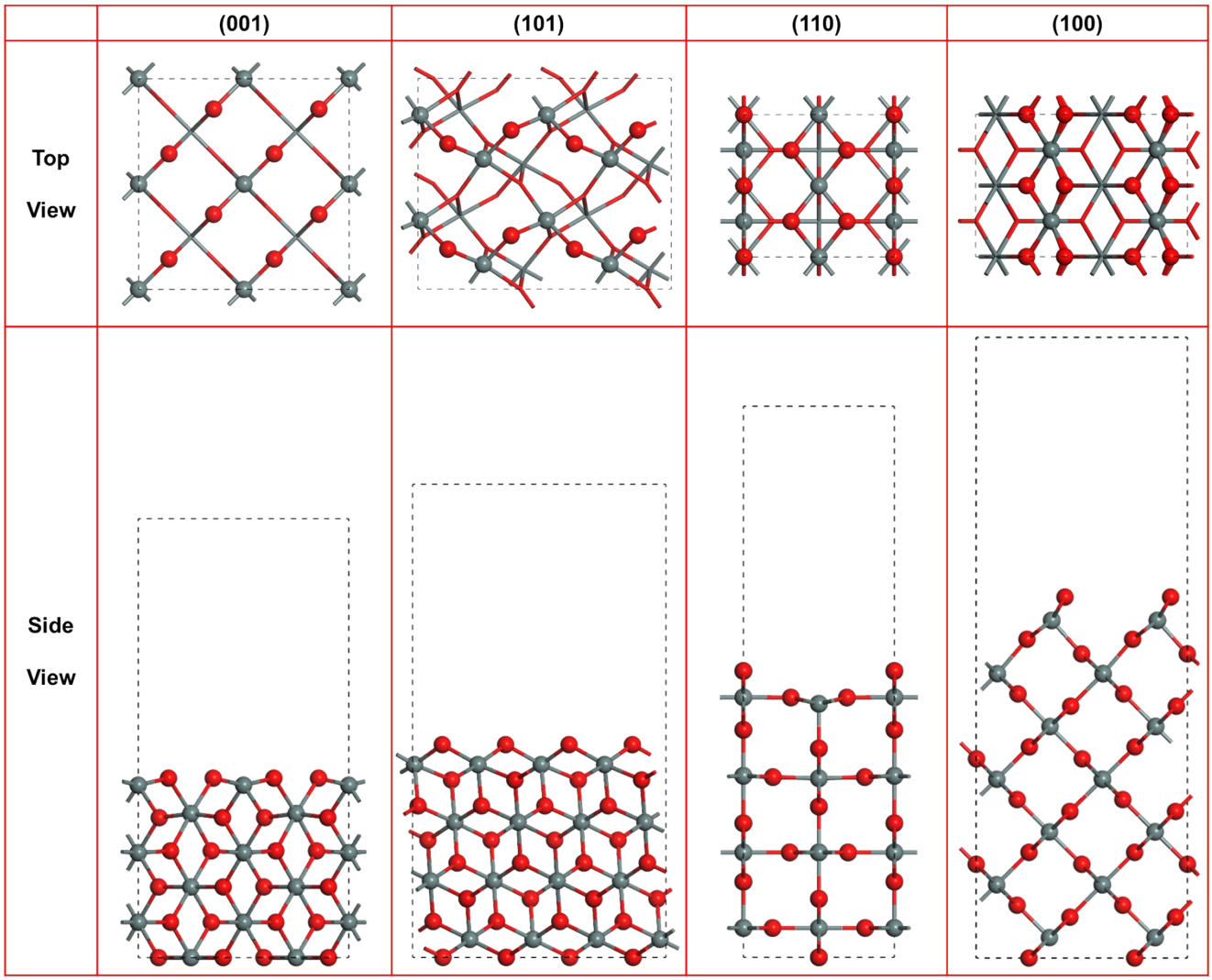


Fig S1. Initial structure of SnO_2 6 layers-(001), 4 layers-(101), 4 layers-(110) and 7 layers-(100) surface.

Table S1. The amounts of impurities that may be present on SnO_2 nanosheets and nanoshuttles.

Sample	Cl / wt %	N / wt %	C / wt %
Nanosheets	< 0.1	< 0.1	< 0.1
Nanoshuttles	< 0.1	< 0.1	< 0.1

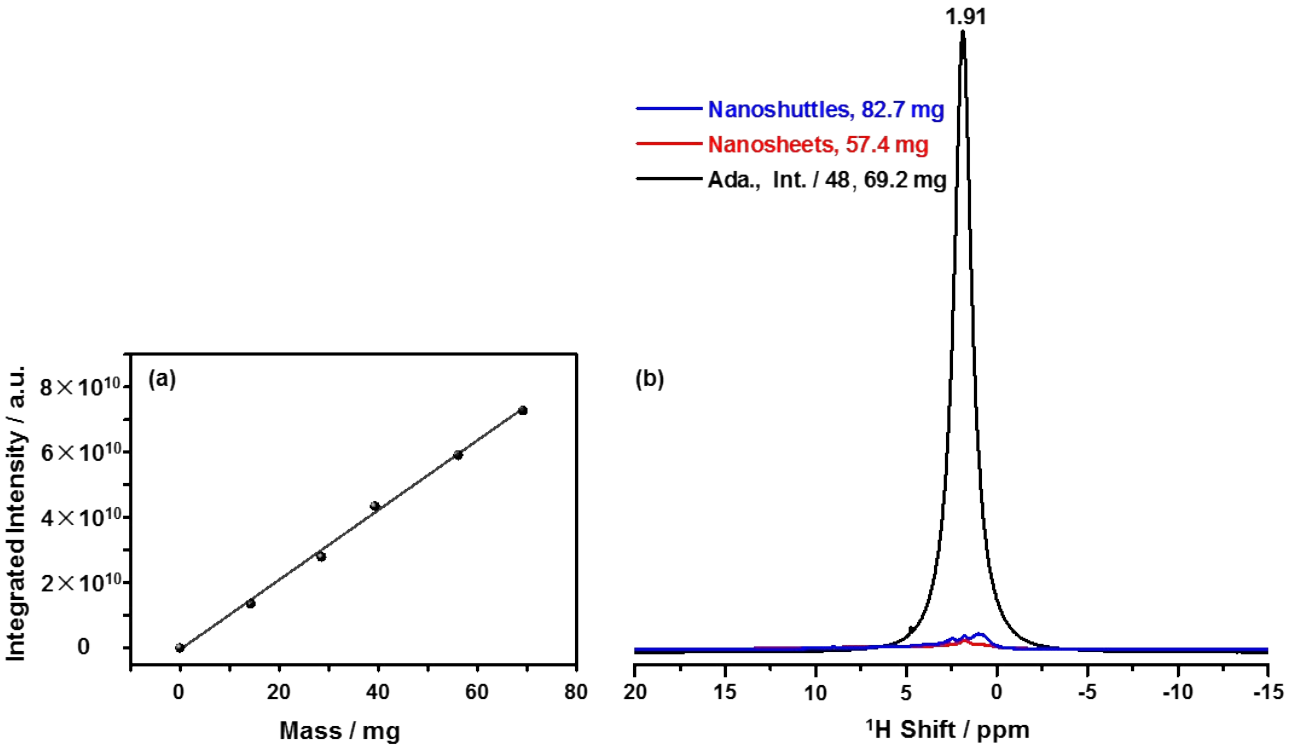


Fig S2. Interpolation method for characterizing the content of hydrogen atoms on SnO_2 nanomaterials from quantitative ^1H NMR, utilizing adamantane (Ada.) as a reference compound. (a) The integrated intensity of ^1H signals as a function from the mass of adamantine packed in the rotor. The integral range is set to 20 ~ -15 ppm. The number of scans acquired was 256 with a spinning speed of 10 kHz. A saturated recycle delay of 32 s was used to guarantee quantitative measurement. The linear correlation between peak intensity (y / a.u.) of the spectra and the mass of adamantine (x / mg) is $y = 1.1 \times 10^9 x - 8.1 \times 10^8$. (b) ^1H NMR spectra of Ada., SnO_2 nanosheets, and SnO_2 nanoshuttles. The same number of scans acquired and spinning speed were used with a saturated recycle delay of 8 s.

Table S2. The concentrations of surface hydrogen of SnO_2 nanosheets and nanoshuttles, respectively. [a]

Sample	Mass / mg	Intensity of 256 Scans / a.u.	Total Amount of Hydrogen / mol·g^{-1}	Concentration of Hydrogen[b] / surface unit^{-1}	Coverage of Hydrogen[c] / %
Adamantane	69.2	7.3×10^{10}	1.2×10^{-1}	/	/
Nanosheets	57.4	1.9×10^{7}	2.1×10^{-6}	0.23	1.84
Nanoshuttles	82.7	3.5×10^{7}	3.8×10^{-6}	0.18	1.44

[a] The concentrations of hydrogen are quantified with the interpolation method employing adamantane as a reference material;

[b] Concentration of Hydrogen (surface unit^{-1}) = Total Amount of Hydrogen (mol·g^{-1}) × N_A / S_{BET} (m^2·g^{-1}) × S_{Unit} (m^2), N_A represents the Avogadro constant (6.02×10^{23} mol^{-1}), S_{BET} is the sample surface area from BET (70.4 m^2·g^{-1} for nanosheets and 117.0 m^2·g^{-1} for nanoshuttles), and S_{Unit} denotes the surface area of one surface unit (78.1 Å^2, the average value of 4 low-index surfaces).

[c] Coverage of Hydrogen (%) = Concentration of Hydrogen (surface unit^{-1}) / 12.5 × 100 %, the constant (12.5) is an average number of surface binding sites on 4 low-index surfaces.

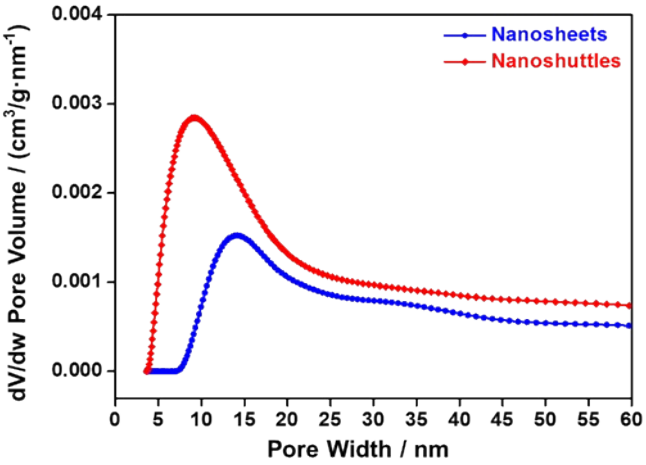


Fig S3. NLDFT pore-size distribution plots of SnO_2 nanosheets and nanoshuttles.

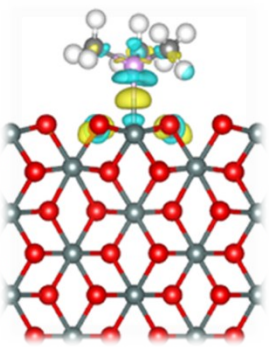
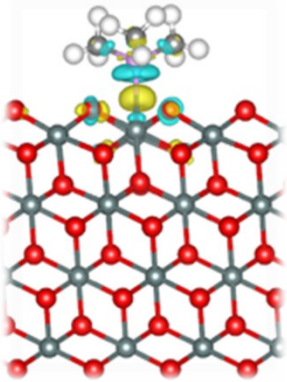
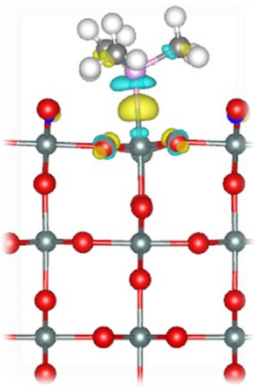
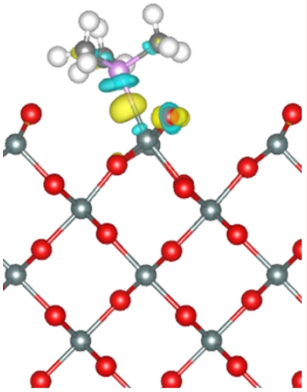
(001): -6 ppm	(101): -14 ppm	(110): -23 ppm	(100): -29 ppm
TMP bonded Sn_{4C}	TMP bonded Sn_{5C}	TMP bonded Sn_{5C}	TMP bonded Sn_{5C}
			

Fig S4. Electron density difference in the acid sites of four facets ((001), (101), (110) and (100)) absorbed with TMP. Yellow area, electron acceptor; Blue area, electron donor.

Table S3. The chemical shifts (δ_{iso}s), peak widths and integrated areas of deconvoluted ^{31}P NMR peaks.

Sample	Facet	(001)	(101)	(110)	(001)
Nanosheets	δ_{iso} / ppm	-6.0	-14.1	-22.5	-29.2
	Width / Hz	1250	1450	1400	720
	Area / %	12.3	38.8	44.2	4.7
Nanoshuttles	δ_{iso} / ppm	-6.0	-14.3	-23.2	-29.0
	Width / Hz	1200	1500	1410	700
	Area / %	2.8	29.4	60.1	10.5