Supporting Information

Ultra-Low-Temperature Ozone Abatement on α-MnO_2(001) Facets with Down-Shifted Lowest Unoccupied Orbitals

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Materials and methods in detail

Catalytic Evaluation. The catalytic performance for ozone removal was evaluated in a fixed−bed quartz reactor (i.d. = 8 mm) under an atmospheric pressure, using 0.2 g catalyst (40−60 mesh) for each run. Data were recorded by a temperature-programmed mode at a ramping rate of 2 ^{o}C min^{-1}. O_3 was generated using ozonator (Guangdong Chuanghuan Ozone Electric Equipment Company, China). The total flow rate through the reactor was maintained at 1.7 L/min (0.5 vol% O_2 and Ar balance) and the inlet ozone concentration maintained at ~60 ppm. The ozone concentration was determined with an ozone analyzer (Model 49i, Thermo Scientific, USA).

Material Characterization. X-ray diffraction (XRD) patterns were obtained at a Rigaku Ultima-IV diffractometer (Japan) with Cu Kα radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) studies were conducted on a JEM 2100F transmission electron microscope. XANES and EXAFS spectra were obtained at the Mn *K*-edges at BL14W of the SSRF with an electron beam energy of 3.5 GeV and a ring current of 200–300 mA. Data were collected with a fixed exit monochromator using two flat Si(111) crystals for the *K*-edge XAS measurements. The raw data were analyzed by using the IFEFFIT 1.2.11 software package. Soft X-ray absorption spectra at the Mn L_3-edges were obtained in a total electron yield (TEY) mode at the 4B9B of the Beijing Synchrotron Radiation Facility (BSRF). X-ray photoelectron (XPS) spectra were obtained at BL 4B9B in the BSRF at a photon energy of 780 eV. All the data were recorded in an ultrahigh vacuum chamber equipped with a VG Scienta R4000 electron energy analyzer with a base pressure of $\sim 4 \times 10^{-11}$ mbar at room temperature. BE of these valence-band spectra were calibrated with respect to the Au $4f_{7/2}$ (BE = 84 eV) featured from a clean gold foil attached to the manipulator. The specific surface areas (SBET) were determined by using linear portion of Brunauer–Emmett–Teller (BET) model. The BET surface areas were measured by N_2 adsorption at a liquid nitrogen temperature using a NOVA4000e (USA, Quantachrome) automated gas sorption system.

Tables and Figures

Table S1. Specific surface areas of α-MnO_2 sheet, α-MnO_2 rod, and β-MnO_2.

Samples	α-MnO_2 sheet	α-MnO_2 rod	β-MnO_2
$S_{BET}/(m^2/g)$	76	59	15

Table S2. EXAFS parameters of α-MnO_2 sheet and α-MnO_2 rod at the Mn *K*-edge.

Samples	Shell	*CN* [a]	*R* [b] / Å	σ^2 [c] / Å^2	ΔE_0 [d] / eV
α-MnO_2 sheet	Mn-O	6	1.90(5)	0.005(7)	2.1
	Mn-Mn	3.2	2.82(4)	0.007(6)	-4.9
α-MnO_2 rod	Mn-O	6	1.88(7)	0.005(3)	-0.1
	Mn-Mn	4	2.90(4)	0.008(3)	0.03

R-space fit, Δk = 2-12.3 Å^{-1}, Δr = 1.1-4 Å;

[a] *CN*, coordination number;

[b] *R*, distance between absorber and backscatter atoms;

[c] σ^2, Debye-Waller factor;

[d] ΔE_0, energy shift.

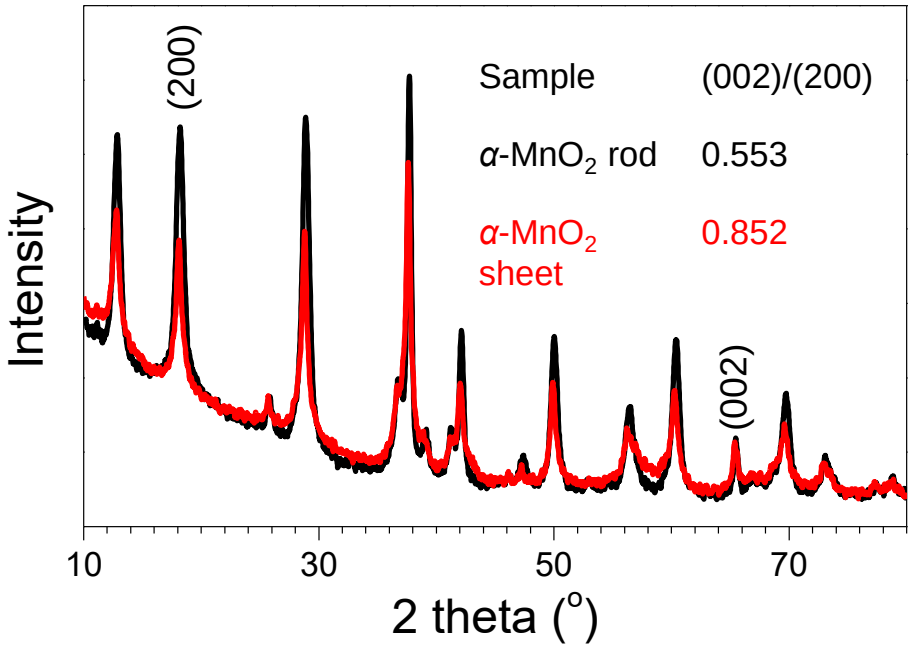

Figure S1. XRD patterns of α-MnO_2 sheet and α-MnO_2 rod. Inset: The ratios of FWHM between (002) and (200) diffraction peaks.

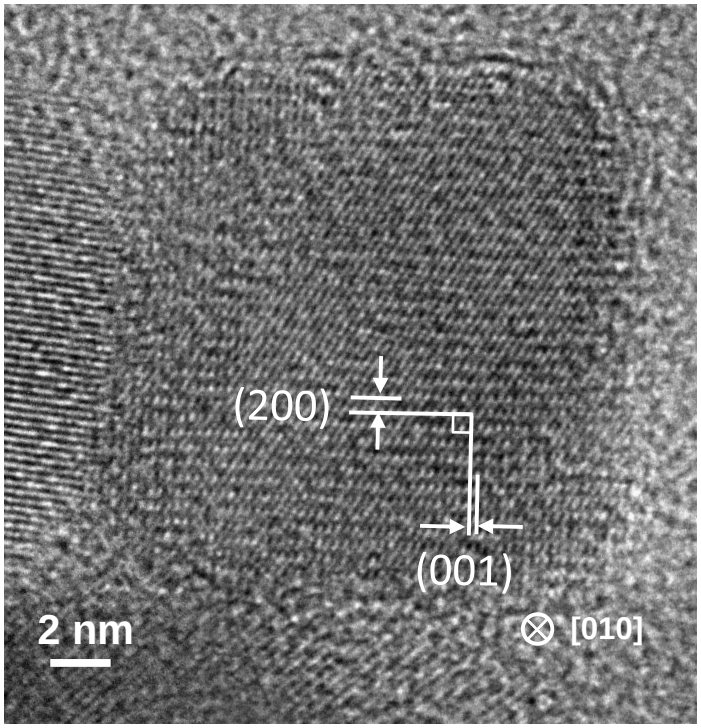

Figure S2. HRTEM image of α-MnO_2 sheets.

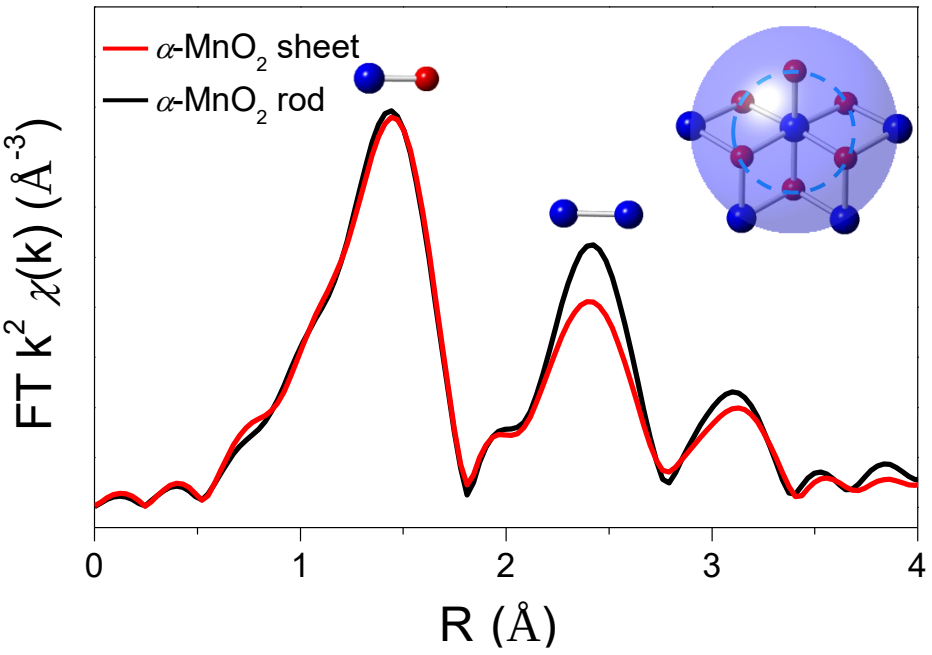

Figure S3. $\chi(R)$ k^2-weighted FT EXAFS spectra at the Mn *K*-edge of α-MnO_2 sheet and α-MnO_2 rod. Blue and red balls represent Mn and O atoms, respectively. The inset models shows four Mn atoms (blue) and six O atoms (red) within a shell with a radius of approximately 3.0 Å of the Mn center.

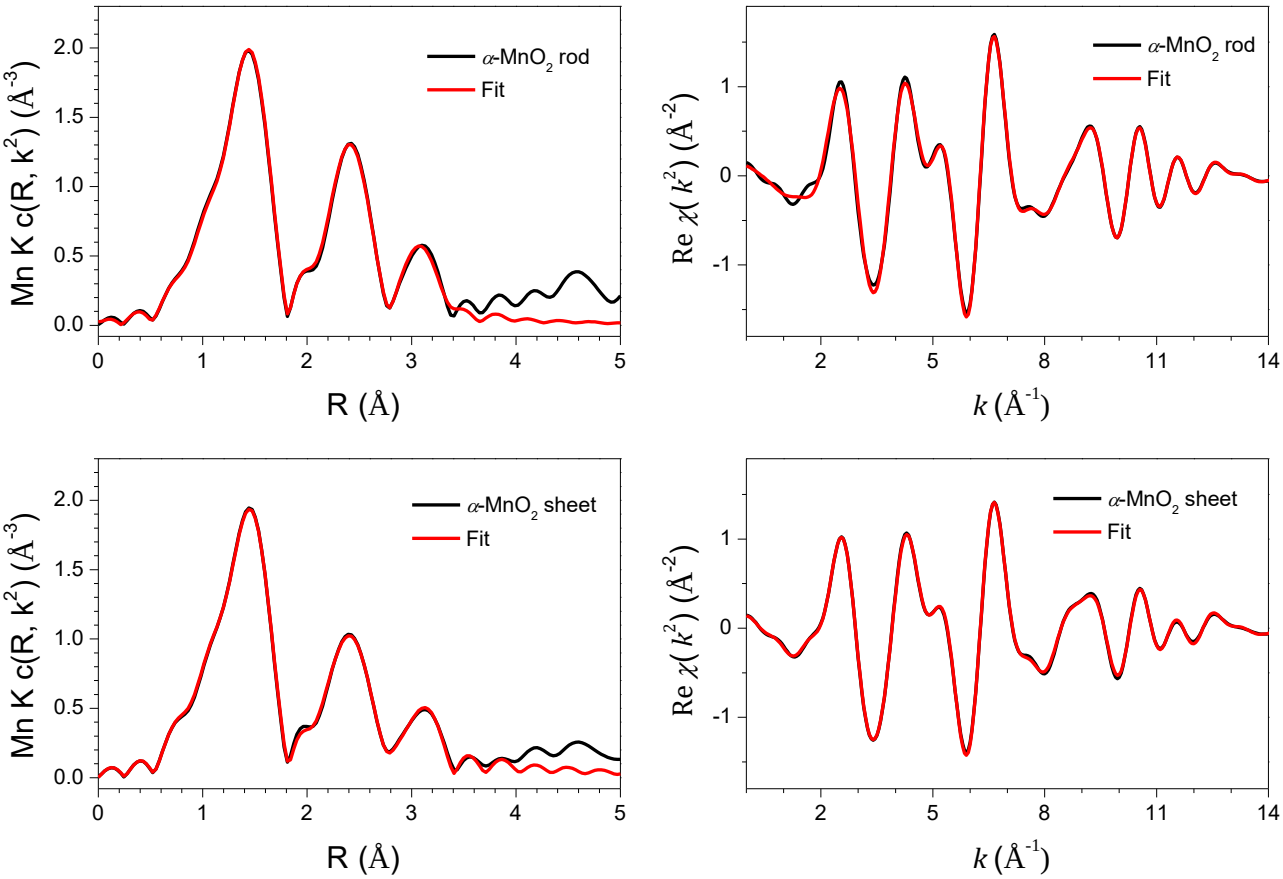

Figure S4. *R*-space (Δk = 2-12.3 Å^{-1}) and inverse FT spectra (Δr = 1.1-4.0 Å) at the Mn *K*-edge of α-MnO_2 sheet and α-MnO_2 rod.

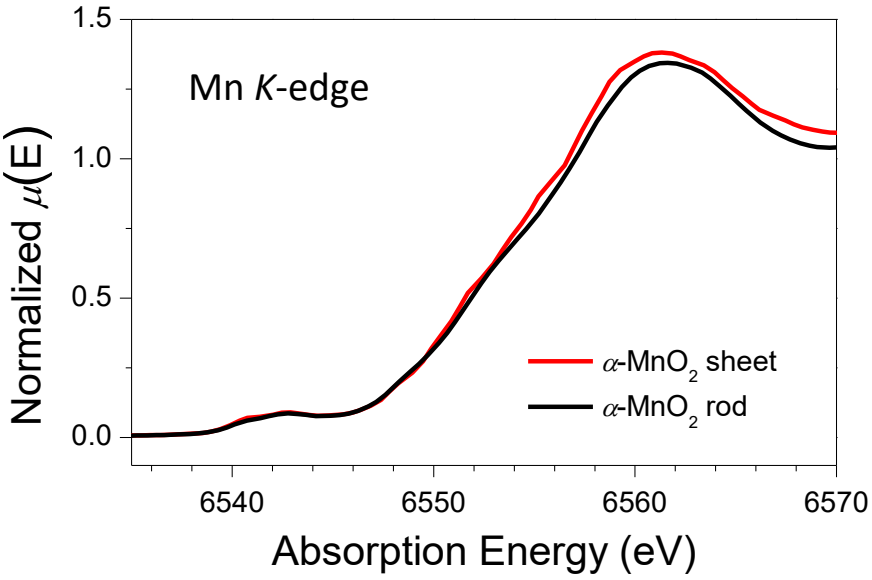

Figure S5. X-ray absorption spectra of α-MnO_2 sheet and α-MnO_2 rod at the Mn *K*-edge.

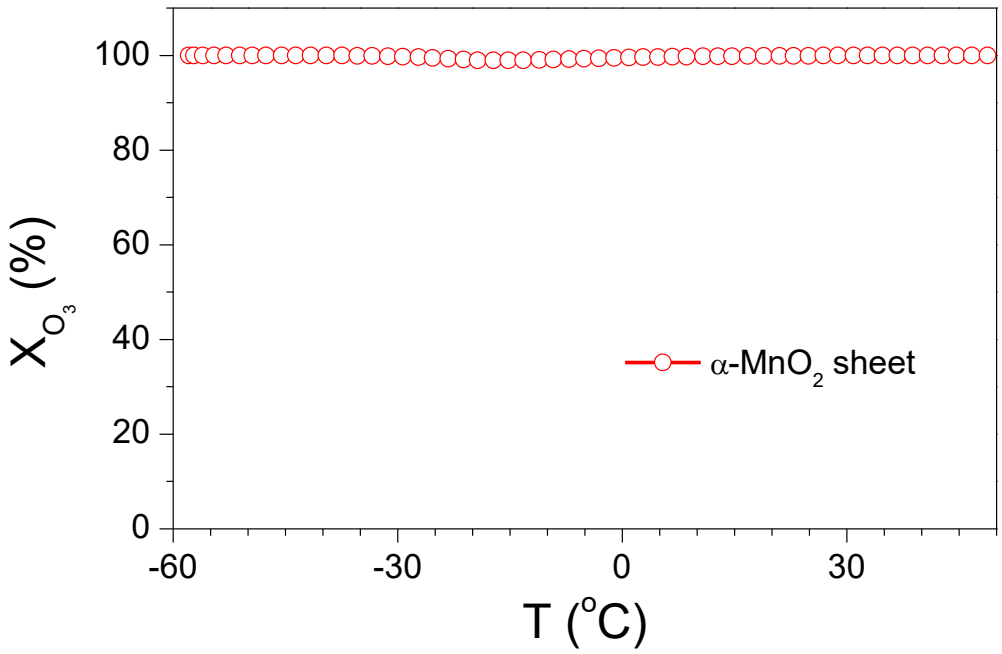

Figure S6. X_{O3} as a function of temperature (T) over α-MnO_2 sheets. Reaction Conditions: 60 ppm O_3, 0.5 vol% O_2 and Ar balance, gaseous hourly space velocity 460,000 h^{-1}.

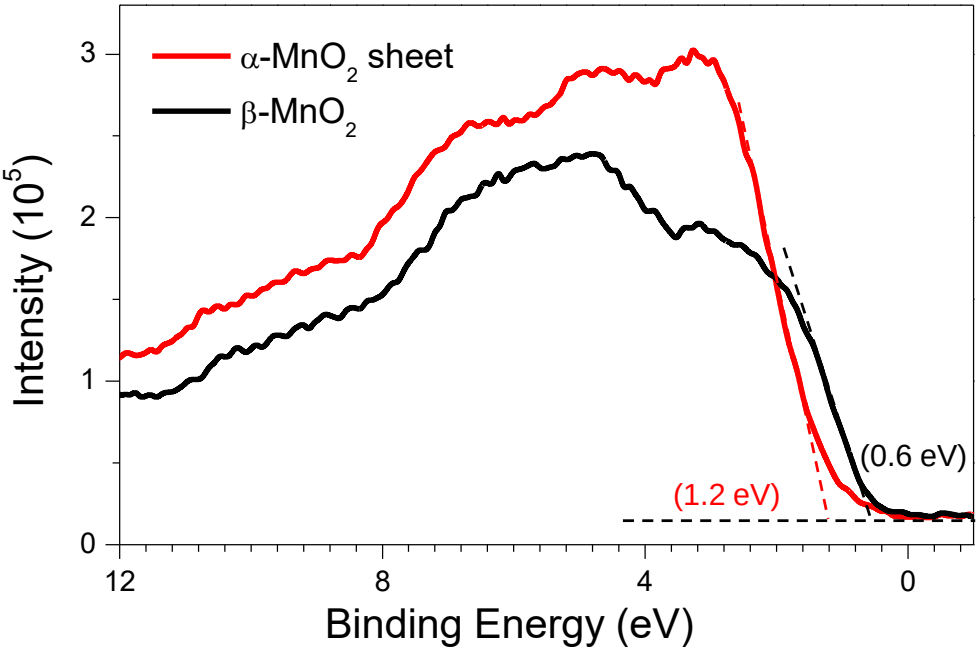

Figure S7. Valence-band XPS of α-MnO_2 sheets and β-MnO_2.