Electronic supplementary information

Adsorption and Oxidation of SO_2 on the Surface of TiO_2 Nanoparticles: The Role of Terminal hydroxyl, Oxygen Vacancy-Ti^{3+} States

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Experimental Section

Chamber experiment

The TiO_2NPs was flattened in a quartz tube in the box. The gas flow rate of SO_2 and O_3 was controlled by mass flow meters. O_3 was generated by O_3 generator and the concentration was monitored by O_3 sensor. The concentrations of SO_2 were controlled at 0.1 ppm (280 μg/m^3), 0.5 ppm (1400 μg/m^3) and 2 ppm (5600 μg/m^3). The chamber RH was controlled *via* introducing humidified N_2 gas that flowed through a tank filled with deionized water. The kinetics of SO_2 oxidation on TiO_2NPs at different time points (10, 20, 30, 120 and 240 min) were studied. All the experiments were operated under ambient pressure at room temperature.

28 Table S1. Positron annihilation lifetimes and intensities of TiO_2NPs analyzed by LT-9 program

Samples	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ns)	I_3 (%)
TiO_2NPs	214 ± 2	59.5 ± 1.3	393 ± 7	38.7 ± 1.3	2.34 ± 0.06	1.79 ± 0.07

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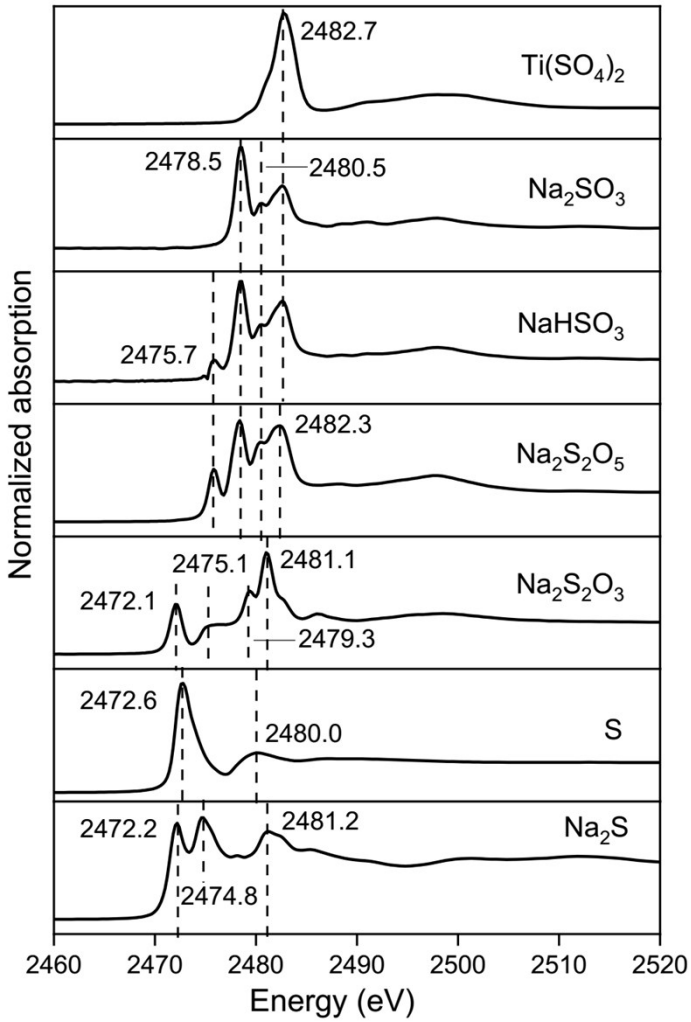


Fig. S1. Sulfur K-edge XANES spectra of S-containing standard references, including titanium sulfate [$Ti(SO_4)_2$], sodium sulfite (Na_2SO_3), sodium bisulfite ($NaHSO_3$), sodium metabisulfite ($Na_2S_2O_5$), sodium thiosulfate ($Na_2S_2O_3$), elemental sulfur (S) and sodium sulfide (Na_2S).

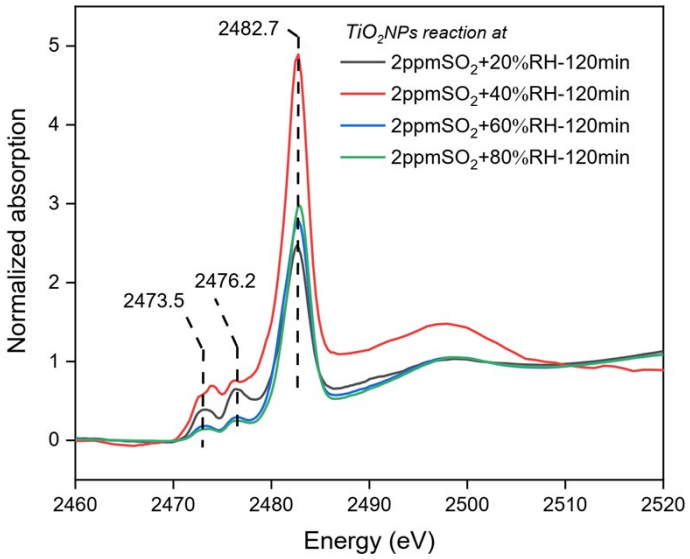
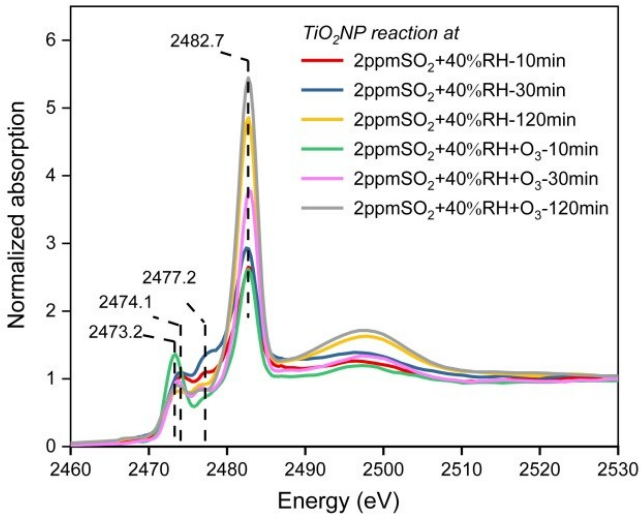


Fig. S2. Sulfur K-edge XANES measurement for the effects of relative humidity (RH) on SO_2 oxidation in TiO_2NPs after 2-ppm SO_2 reaction with TiO_2NPs for 120 min.

(A)



(B) Quantitative analysis of sulfur chemical species on TiO_2NPs when O_3 co-presence

TiO_2NP reaction at	Sulfite/Bisulfite	Sulfate
2ppmSO_2+40%RH-10min	11.5	88.5
2ppmSO_2+40%RH-30min	8.3	91.7
2ppmSO_2+40%RH-120min	3.4	96.6
2ppmSO_2+40%RH+O_3-10min	9.9	90.1
2ppmSO_2+40%RH+O_3-30min	7.3	98.8
2ppmSO_2+40%RH+O_3-120min	2.4	99.4

(C)

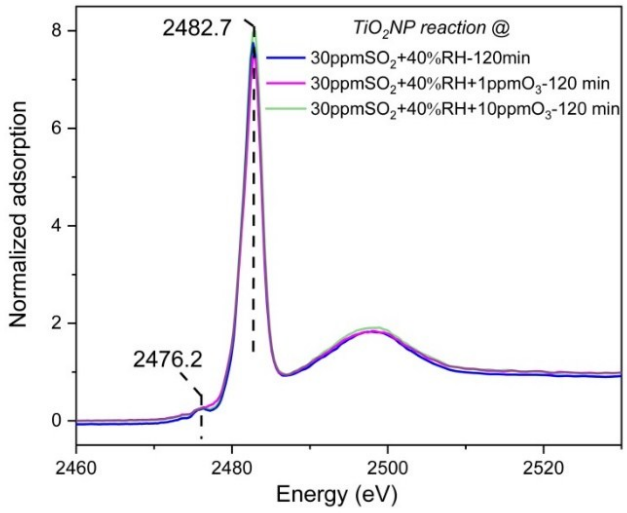
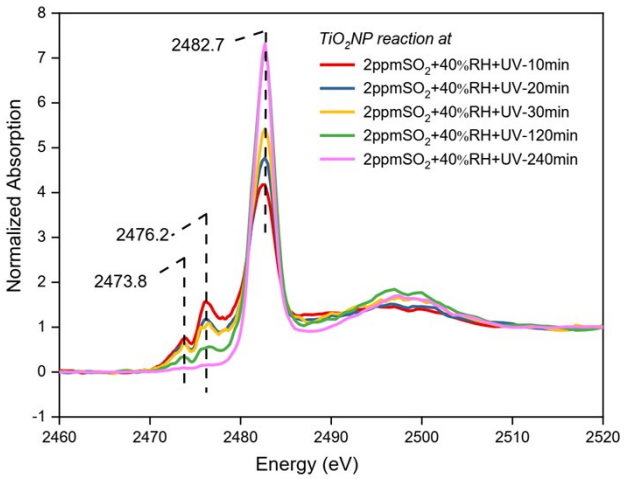


Fig. S3. Sulfur K-edge XANES measurement for SO_2 oxidation on TiO_2NPs (at 40% RH) when 1 ppm and 10 ppm O_3 copresence.

(A)



(B) Quantitative analysis of S chemical species on TiO_2NPs

Reaction time	Sulfite/Bisulfite	Sulfate
10min	6.9	93.1
20min	4.4	95.6
30 min	2.8	97.2
120 min	1.1	98.9
240 min	0.1	99.9

Fig. S4. Sulfur K-edge XANES measurement for the effects of UV-irradiation time on SO_2 oxidation in TiO_2NPs after reactions (at 40% RH).