

Supporting Information

Photocatalytic oxidation of SO₂ by TiO₂: Aerosol formation and key role of gaseous reactive oxygen species

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EXPERIMENTAL METHODS

Pre-treatment of TiO₂

First, TiO₂ was calcined at 673K in a muffle furnace. Then, 100 ± 1 mg TiO₂ was dispersed in 5 mL deionized water with 15 min ultrasound treatment. After that, the suspension of TiO₂ was coated on glass plate and dried with gentle zero air. When the film of TiO₂ was formed, the coated glass plate was dried at 473 K for 2 h in an oven. Then put the cooled glass plate into reactor and fixed it. The reactor was washed with zero air for several times after that. At last, lights in smog chamber were turned on for 11 h to further purify the coated TiO₂.

Aerosol yields calculation

With the input of aerosol density (ρ , g/cm³) as illustrated in table S1, number concentration, mass concentration, diameter distribution of aerosol could be direct obtained from the output of SMPS data. The SA_g-H₂SO₄ (m_{net} , µg/m³) was calculated from the mass concentration of SA_g (m_{aerosol} , µg/m³) and the ratio of H₂SO₄ in aerosol (γ) as shown in equation 1. The yields of SA_g (Y_{aerosol} , %) and SA_g-H₂SO₄ (Y_{net} , %) were calculated with equation 2, where ΔSO_2 was the consumed SO₂ concentration (ppbv), M_{SO_2} (g/mol) was the molar mass of SO₂ and A was the molar gas volume. The ratio of SO₂ oxidized in gas phase (α) was calculated from equation 3, where $M_{\text{H}_2\text{SO}_4}$ was the molar mass of H₂SO₄.

$$m_{\text{net}} = m_{\text{aerosol}} \times \gamma \quad (1)$$

$$Y_{\text{aerosol/net}} = \frac{A \times m_{\text{aerosol/net}}}{M_{\text{SO}_2} \times \Delta\text{SO}_2} \times 100\% \quad (2)$$

$$\alpha = \frac{m_{\text{net}} \times A}{M_{\text{H}_2\text{SO}_4} \Delta\text{SO}_2} \times 100\% \quad (3)$$

Flow tube experiment with SO₄²⁻ pre-treated TiO₂

The flow tube experiment was also performed with sulphate pre-treated TiO₂. Sulfate was pre-adsorbed on the coated TiO₂ via the photodegradation of SO₂ in the illumination of UV-light. Sulfate adsorbed on the surface of TiO₂ in physical and weak chemical way was swept off with

zero air in a fast flow rate. Thus, the remaining sulfate on TiO₂ surface was hardly removed. Then, the pre-treated TiO₂ would be used for all RH conditions experiments.

Simulation of H₂SO₄ formation

According to the results from chamber experiments, we simulated the formation of SA_g-H₂SO₄ in real atmosphere. It is assumed that the generated gaseous ROS radical and the formed active sites on a unit area were considered as B and C. It was assumed that B and C almost keep constant at a certain RH condition. The generated ROS spread into gas phase. Equation 4 showed the formation rate of H₂SO₄ in gas phase. The reaction rate of SO₂ participating in heterogeneous reaction could be calculated from equation 5.

$$\frac{dH_2SO_4}{dt} = k_1 \times \frac{S \times B}{V} \times C_{SO_2} \quad (4)$$

$$\frac{dSO_4^{2-}}{dt} = \gamma \times \frac{f \times S}{4} \times C_{SO_2} = k_2 \times C \times S \times C_{SO_2} \quad (5)$$

Where k_1 was a coefficient related to reaction rate coefficient of SO₂ with ROS, and S , V were TiO₂ surface area and volume of space, respectively. SO₂ oxidization in gas phase should be positive with the TiO₂ surface area and gaseous ROS formation, but negative with the V . γ was the uptake coefficient of SO₂ on TiO₂ and was closely related to active sites formation (C). f was denoted as the mean thermal velocity of SO₂. k_2 was an apparent coefficient.

Hence, the ratio of SO₂ oxidized in gas phase (α) should obey the rule of equation 6.

$$\alpha = \frac{dH_2SO_4}{dt} / \left(\frac{dSO_4^{2-}}{dt} + \frac{dH_2SO_4}{dt} \right) = \frac{k_1 B}{k_1 B + k_2 V C} = \frac{1}{1 + \frac{k_2 C}{k_1 B} V} = \frac{\frac{1}{V}}{\frac{1}{V} + \frac{k_2 C}{k_1 B}} \quad (6)$$

Divide equation 4 and 5 on both sides,

$$\frac{dH_2SO_4}{dt} / \frac{dSO_4^{2-}}{dt} = \frac{k_1 B}{k_2 C V} \quad (7)$$

$\frac{k_1 B}{k_2 C V}$ represents the ratio of SO₂ oxidized in gas phase to SO₂ oxidized on the surface. In our experiment, V was 1200 L. Then, $\frac{k_1 B}{k_2 C}$ could be calculated from the value of α in Table S1. Because $\frac{k_1 B}{k_2 C}$ was affected by RH, gaussian fitting was performed to cover the whole range of RH. The gaussian fitting result was illustrated in Figure S10, and the simulation equation was shown in

equation 8. Input the value of $\frac{k_1B}{k_2C}$ at various RH (%) and space condition, α in real environment was calculated. Finally, H_2SO_4 aerosol formation could be calculated from equation 9, where A was the molar gas volume, ΔSO_2 was the consumed concentration of SO_2 (ppbv), $m_{H_2SO_4}$ was the mass concentration of generated H_2SO_4 aerosol, $M_{H_2SO_4}$ was the molar mass of H_2SO_4 . Because when the concentration of generated H_2SO_4 reached 7×10^6 molecule cm^{-3} (much small than 1ppbv)²⁶, H_2SO_4 aerosol start to form. We assumed that the SO_2 oxidized in gas phase almost totally transformed into H_2SO_4 aerosol.

$$\frac{k_1B}{k_2C} = 0.2414 \times e^{(-(RH-13.29)/7.051)^2} + 0.134 * e^{(-(RH-78.22)/92.26)^2} \quad (8)$$

$$m_{H_2SO_4} = \alpha \times \frac{\Delta SO_2}{A} \times M_{H_2SO_4} \quad (9)$$

In real atmosphere, multiple oxidation pathways could contribute to the oxidation of SO_2 . If the proportion of SO_2 oxidized from the photocatalytic process could be calculated, the contribution of the photocatalytic process to H_2SO_4 formation could be obtained. The photocatalysis rate of SO_2 in our photocatalysis experiment was $0.59 \pm 0.03 \text{ h}^{-1}$. There was a positive correlation between the photocatalysis rate and the surface area concentration of TiO_2 coating in smog chamber. The coated area of TiO_2 on glass plate was $25 \text{ cm} \times 28.5 \text{ cm}$ and the volume of smog chamber was 1.2 m^3 . Then, the photocatalysis rate of SO_2 (k) should be equal to $(2.8 \pm 0.1) \times 10^{-1} \text{ s}^{-1} \text{ cm}$. The consumption rate of SO_2 by the photocatalysis process could be expressed by equation 10, where S_c is the complete surface area, V is the volume of space, j was the proportion of TiO_2 coating area to the complete surface area, S_g is the ground area and H is boundary height. The obtained parameters in our study could be used in model to further simulate the oxidation of SO_2 and the formation of H_2SO_4 aerosol in complex real atmosphere.

$$-\frac{dSO_2}{dt} = k \times \frac{S_c}{V} \times j = k \times \frac{S_c}{S_g \times H} \times j \quad (10)$$

Results of Smog Chamber Experiments

The detail results of the photocatalysis of SO₂ by TiO₂ in smog chamber are shown in Table S1. The ρ was input as parameter into SMPS, which was obtained from previous studies¹. The directly detected mass concentration of SA_g included H₂SO₄ and H₂O, which was illustrated in Figure S4. The yields of SA_g ranged from 10.10% to 68.28%, which were calculated from the slope fitted in Figure S4. Excluding the influence of H₂O, the mass concentration of SA_{g-H2SO4} was obtained from the product of the mass concentration of aerosol and the ratio of H₂SO₄ in aerosol (γ)¹. The formation of SA_{g-H2SO4} was shown in Figure S5. The yields of SA_{g-H2SO4} ranged from 10.10% to 32.64%. The different colors in Figure S4 and Figure S5 represent the repeated experiments.

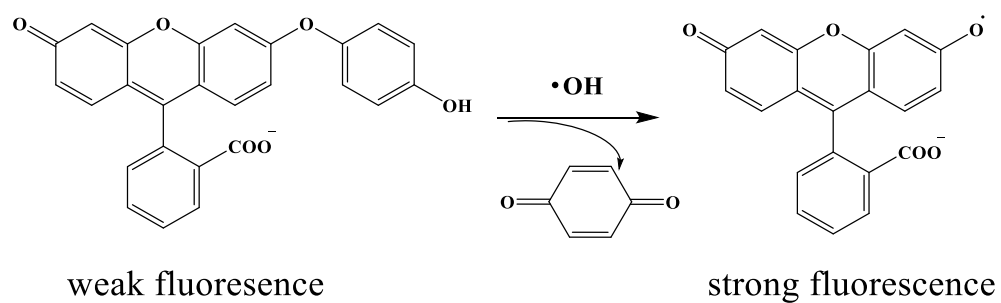
Table S1. Experimental setups and results of SO₂ photocatalyzed by TiO₂ at various RH conditions

RH (%)	ρ (g/cm ³) ¹	Ratio of H ₂ SO ₄ in aerosol γ ¹	RH (%)	SO ₂ (ppb)	aerosol yield (%) ^[a]	H ₂ SO ₄ yield (%) ^[a]	The ratio of SO ₂ oxidized in gas phase α ^[a]
1%	1.8	1	<1%	30	7.52±0.95	7.52±0.95	4.91±0.62
			<1%	29	7.95±1.15	7.95±1.15	5.19±0.75
			<1%	40	10.41±1.32	10.41±1.32	6.80±0.87
			<1%	43	12.39±1.45	12.39±1.45	8.09±0.95
			1.5	43	12.25±1.42	12.25±1.42	8.00±0.92
			average		10.10±2.30	10.10±2.30	6.60±1.50
5%	1.7	0.72	6.1	43	22.35±2.45	16.40±2.01	10.71±1.31
			5.1	41	25.32±2.85	18.23±2.05	11.91±1.34
			4.7	43	25.50±2.91	18.53±2.12	12.10±1.38
			5.6	43	26.74±2.97	19.38±2.23	12.66±1.46
			average		24.98±1.86	18.13±1.26	11.84±0.82
10%	1.6	0.7	10.8	16	43.90±5.17	30.73±3.62	20.07±2.37
			10.7	27	44.17±5.09	30.92±3.56	20.19±2.33
			9.3	40	47.24±5.31	33.07±3.72	21.59±2.43

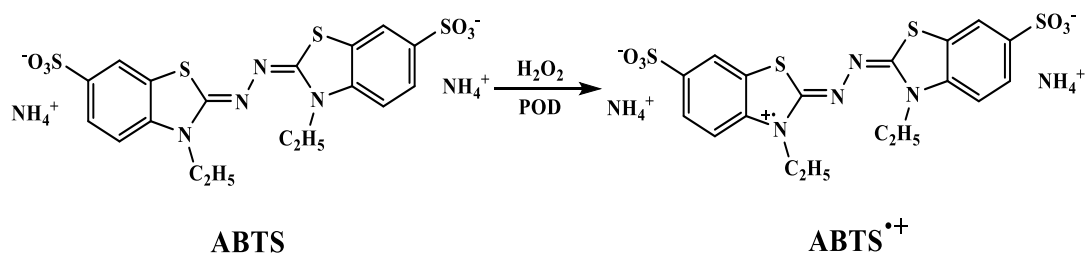
20%	1.5	0.6	11.5	40	51.22±6.12	35.86±4.28	23.42±2.8
			average		46.63±3.42	32.64±2.39	21.32±1.56
			21.2	33	31.41±3.53	18.85±2.12	12.31±1.38
			19.3	35	45.21±5.26	27.13±3.15	17.72±2.06
			21.0	34	42.86±5.12	25.72±3.07	16.79±2.01
			19.2	35	41.11±4.68	24.67±2.81	16.11±1.83
30%	1.4	0.54	average		40.15±6.06	24.09±3.64	15.73±2.38
			28.6	39	28.59±3.16	15.44±1.70	10.08±1.11
			29.8	49	33.06±3.69	17.85±1.99	11.66±1.3
			31.2	45	29.95±3.28	16.17±1.77	10.56±1.16
			29.4	42	27.30±2.94	14.74±1.59	9.63±1.04
			average		29.73±2.47	16.05±1.34	10.48±0.87
50%	1.3	0.45	53.0	41	30.84±3.37	13.88±1.51	9.06±0.99
			53.7	39	33.11±3.67	14.90±1.65	9.73±1.08
			43.1	48	35.74±3.96	16.08±1.78	10.50±1.16
			59.6	48	32.54±3.89	14.64±1.75	9.56±1.14
			average		33.06±2.03	14.88±0.91	9.72±0.60
			76.3	62	52.90±5.84	14.28±1.58	9.33±1.03
70%	1.2	0.27	75.9	43	80.39±9.45	21.49±2.99	14.04±1.94
			73.8	43	88.78±9.87	23.97±2.66	15.65±1.74
			71.5	47	51.05±5.99	13.78±1.62	9.00±1.06
			average		68.28±19.1	18.38±5.13	12.00±3.35
				5			

^[a]: the stated uncertainties included 10% system error and the standard error of fitting.

Scheme S1. The reaction between HPF and OH radical.



Scheme S2. the reaction between ABTS and H₂O₂ in the presence of POD.



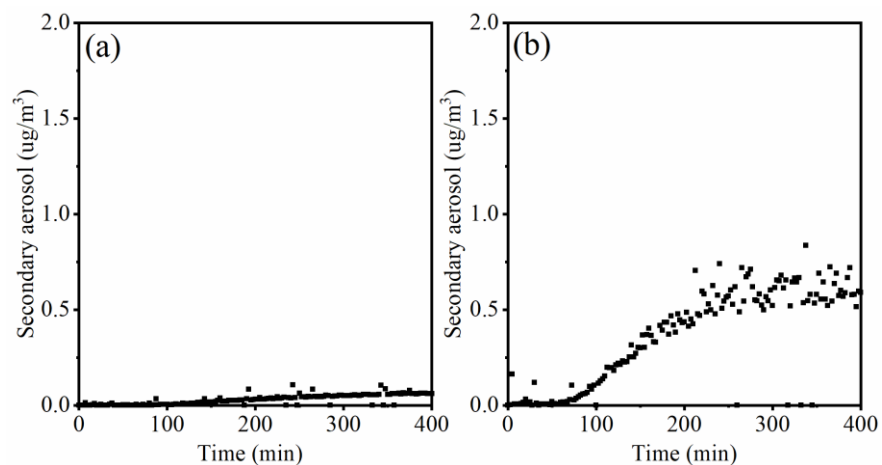


Figure S1. Secondary aerosol formation in the photolysis of SO_2 at RH 1% (a) and 30% (b).

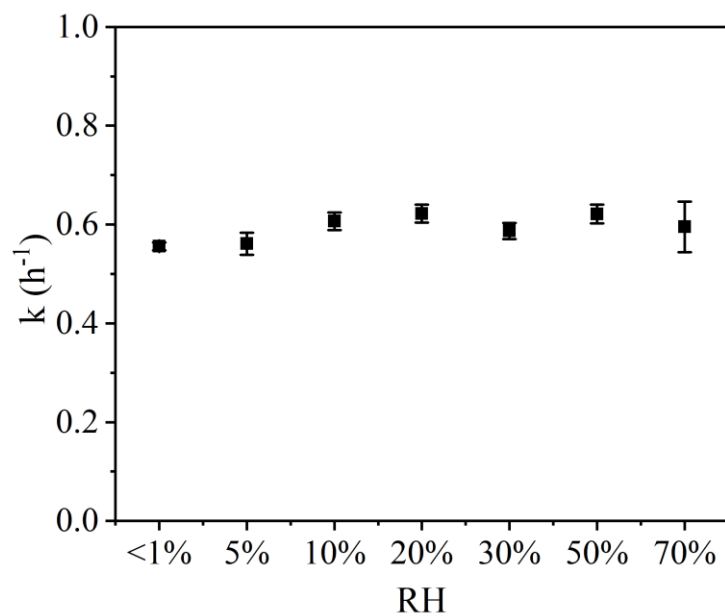


Figure S2. Reaction rate of the photocatalysis of SO_2 by TiO_2 at various RH condition.

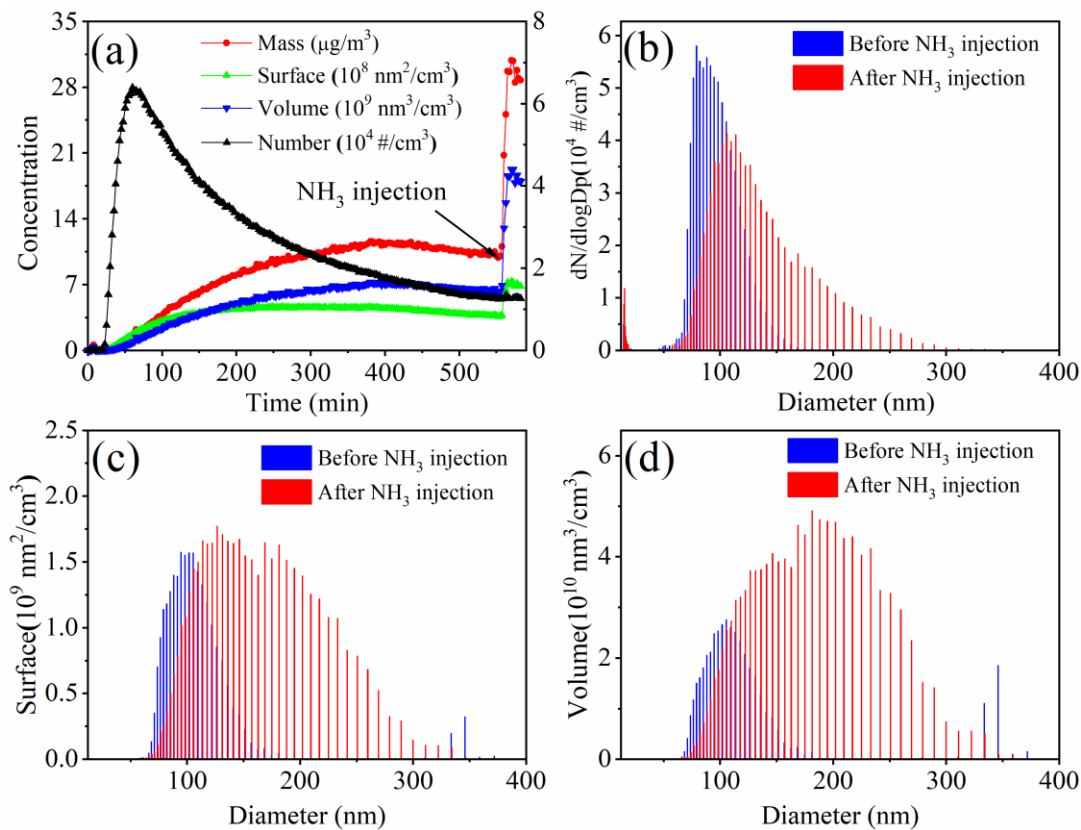


Figure S3. Evolution of SA_g including total mass, total surface, total volume, and total number concentration (a), the comparison of the distribution of number concentration (b), surface concentration (c), and volume concentration (d) before NH_3 injection and after NH_3 injection.

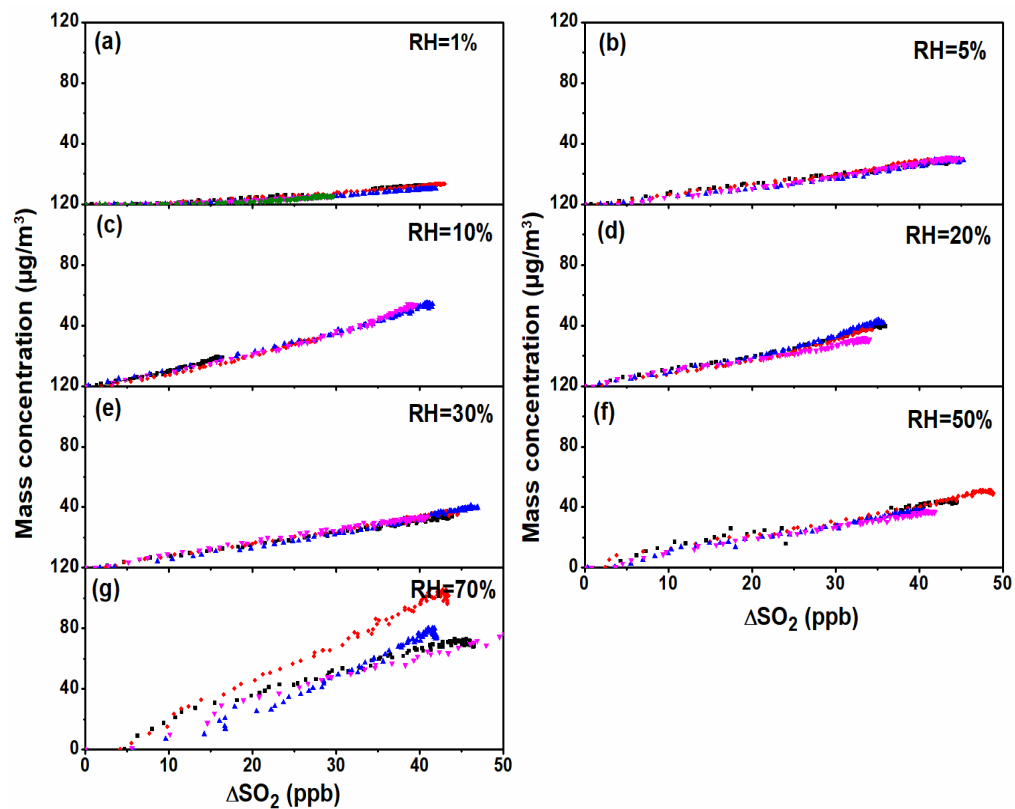


Figure S4. Formation of SA_g in the photocatalysis of SO_2 by TiO_2 at different RH, (a)、(b)、(c)、(d)、(e)、(f)、(g) represent the results at RH 1%、5%、10%、20%、30%、50% and 70%, respectively. The different colours represent the repeated experiments.

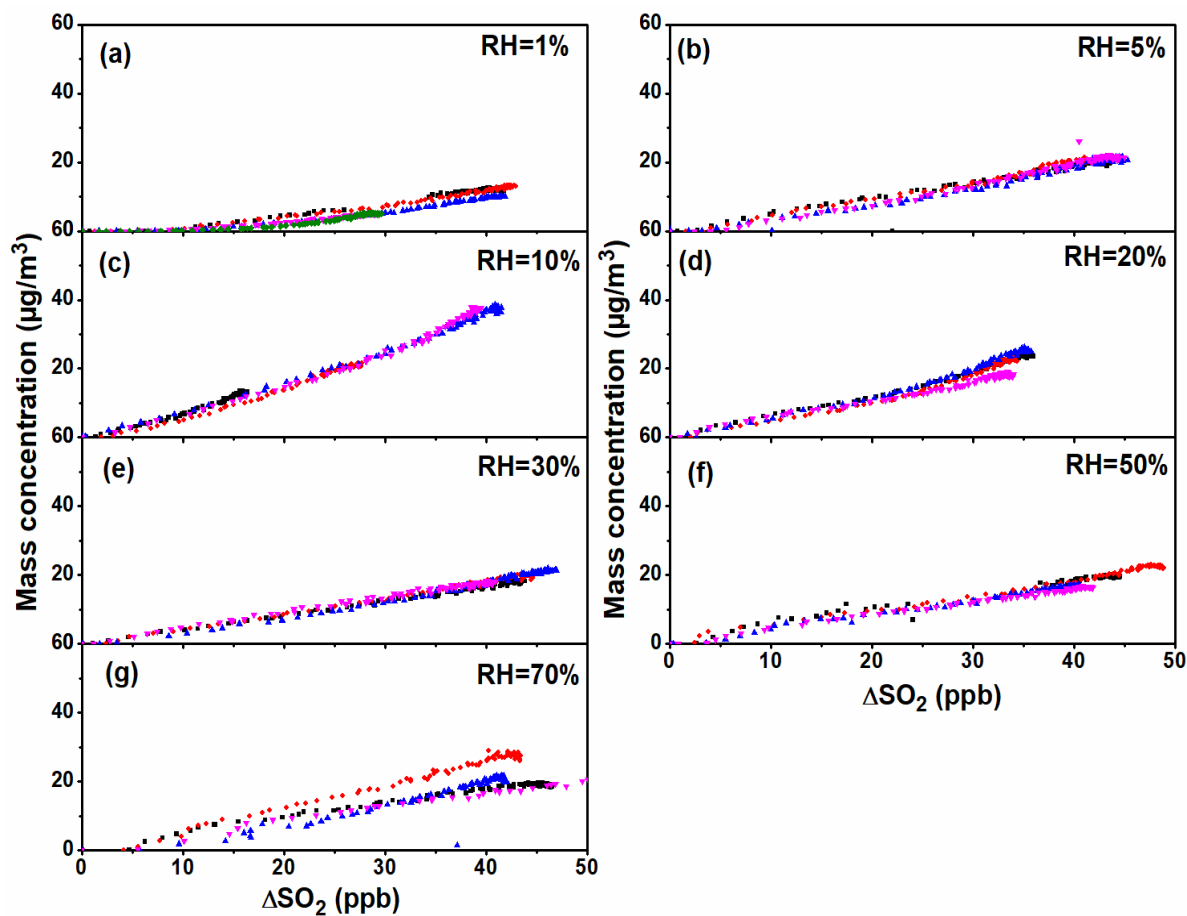


Figure S5. Formation of $\text{SA}_g\text{-H}_2\text{SO}_4$ in the photocatalysis of SO_2 by TiO_2 at different RH, (a)、(b)、(c)、(d)、(e)、(f)、(g) represent the results at RH 1%、5%、10%、20%、30%、50% and 70%, respectively. The different colours represent the repeated experiments.

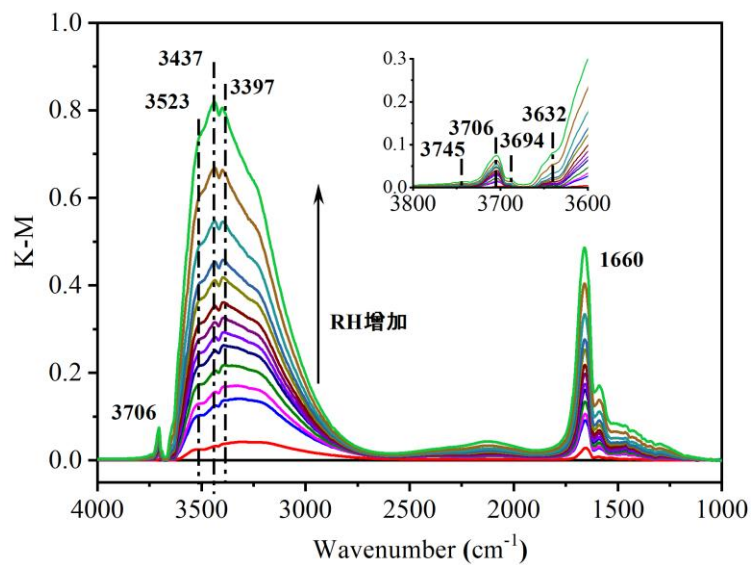


Figure S6. The adsorption of H₂O on TiO₂ under dark condition

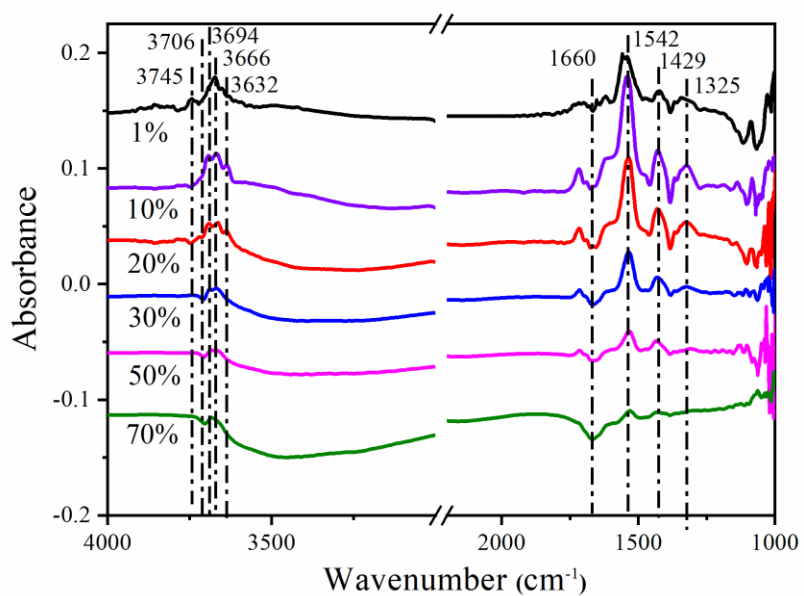


Figure S7. DRIFTS spectra of the photocatalysis of H₂O by TiO₂ under different RH condition.

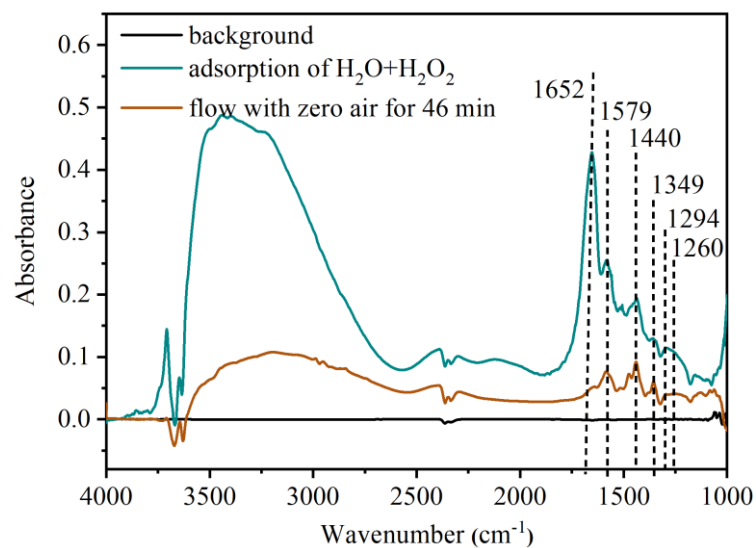


Figure S8. DRIFTS spectra of the adsorbed H_2O_2 (30% in H_2O) on TiO_2 .

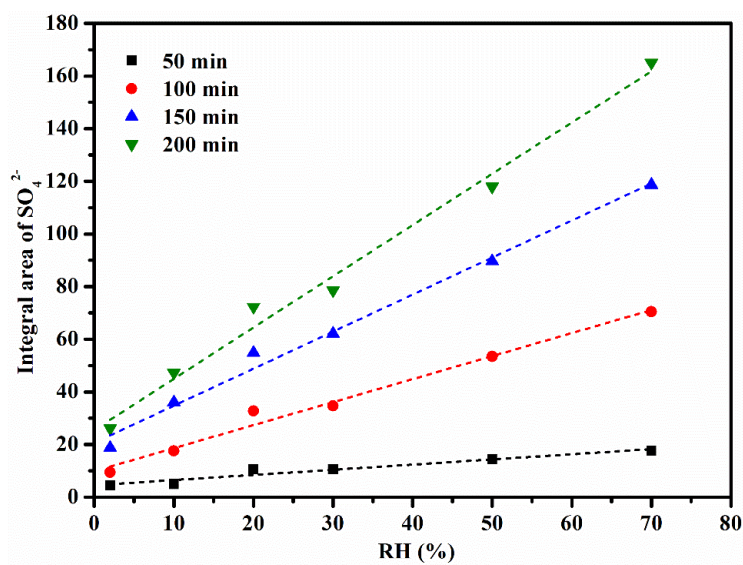


Figure S9. Evolution of the integral areas of SO_4^{2-} on TiO_2 at various RH conditions.

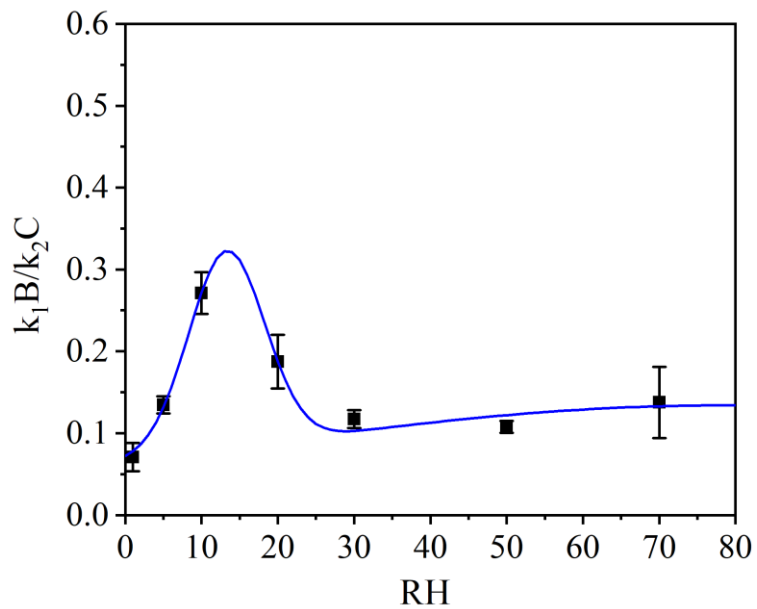


Figure S10. Gaussian fitting of the proportion of SO₂ oxidized in gas phase with the increase of RH.

References

(1) Seinfeld, J. H.; Pandis, S. N., Atmospheric Chemistry and Physics: From Air Pollution to Climate Change; John Wiley & Sons, 2016.