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## Supporting Information

# Atmospheric Organic Complexations Enhanced Sulfate Formation and Iron Dissolution on Nano α-Fe<sub>2</sub>O<sub>3</sub>

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#### Text S1

#### The oxalate consumption

As discussed earlier, the presence of low to moderate amount of oxalate on the surface of hematite nanoparticles could evidently promote the heterogeneous SO<sub>2</sub> uptake under light illumination, owing to the formed iron-oxalate complexes with strong photochemical reactivity. In the meantime, the oxalate might be oxidized to some other species like monoacids, CO<sub>2</sub> and H<sub>2</sub>O. Through the IC analyses, the concentrations of formic acid and acetic acid were inconspicuously changed, probably owing to the slight oxalate consumption and high vapor pressure of the two monocarboxylic acids. Thus, the products of oxalate photooxidation were not analyzed in detail, and only the concentration variations were investigated. Under dark condition (data not shown), there was hardly any change of oxalate concentration, indicating that the oxalate did not essentially participate in SO<sub>2</sub> heterogeneous oxidation and the gases flow could not blow off the tightly chemisorbed oxalate. Under light irradiation, it was found that a certain amount of oxalate was consumed during  $SO_2$ heterogeneous uptake, owing to the photochemical reactions.<sup>1</sup> Specifically, as displayed in Fig. S4a, it could be observed that the consumption of oxalate was evidently increased while the sulfate production was suppressed with increasing the mass fraction of oxalate (> 6.23%), which might be because that excessive oxalate would compete ROS for self-oxidation.<sup>2</sup> The slightly improved sulfate production with obviously enhanced oxalate depletion under stronger light irradiation might also be resulted from the oxalate self-oxidation (Fig. S4b). Furthermore, the consumed amount of oxalate was continuously increased with increasing RH (Fig. S4c), which was almost consistent with the change tendency of sulfate production, suggesting that higher RH was favorable to the ROS generation and the produced ROS was mainly employed for S(IV) oxidation. Meanwhile, the results

indirectly implied that the prevented sulfate formation at RH of ~85.1% was due to the competitive adsorption between  $SO_2$  and water molecules. Besides, the oxalate consumption was also observed in ATD-oxalate system under solar light irradiation (Fig. S4d). Herein, the results suggested that the heterogeneous photochemistry on iron-oxalate complexes could enhance  $SO_2$  heterogeneous conversion and which might also be a sink of atmospheric DCAs.

Additionally, there was no obvious concentration change of malonate and succinate under dark and light illumination (data not shown), likely because of the negligible depletion and inferior photochemical reactivity.



Fig. S1 The schemes for HO-x films preparation.



Fig. S2 The standard curve of total Fe concentration vs. absorbance at 510 nm.



Fig. S3 The SEM image of ATD particles.



Fig. S4 The oxalate consumption during heterogeneous  $SO_2$  conversion under different conditions. (a) the impacts of oxalate mass fraction, (b) the influence of light intensity on HO-6.23, (c) the effects of RH on HO-6.23, and (d) the oxalate depletion on ATD-oxalate systems.



Fig. S5 The sulfate formation on ATD containing oxalate with different mass fraction under dark and light irradiation.



**Fig. S6** The in-situ DRIFTs spectra as a function of time (60 min reaction). (a) and (b) K-M spectra obtained from HO-0 and HO-6.23 mixture, respectively. (c) the calculated ions of sulfur-containing species and uptake coefficients from the two systems, and (d) the comparison of DRIFTs spectra obtained at 60 min in the presence or absence of oxalate.



Fig. S7 (a) The enhancement factors of oxalate on iron solubility and (b) the influences of relative humidity.

### References

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