June 21, 2022

Editor-in-Chief, Atmospheric Chemistry and Physics

Dear Prof. Ryan Sullivan:

Thank you very much for your kind consideration on our paper "The Positive Effect of Formaldehyde on the Photocatalytic Renoxification of Nitrate on TiO_2 Particles" (Manuscript ID: Preprint acp-2022-6).

Thanks for the reviewer' comments, which are valuable and helpful for revising and improving the manuscript. In the revised manuscript, we have considered the reviewer' comments in detail and made revisions accordingly, which were highlighted with the red color. In particular, we redrew the size distribution of 4 wt.% KNO_3-TiO_2 and TiO_2 and plotted them together with suitable symbols size, as seen in Figure S3, and the description was added in the new revised manuscript in section 2.3. This results indicate that the repeatability of the introduction of particles into the chamber is good and the comparison among different samples in our study is reliable. We addressed the reviewer's questions point-by-point carefully in the response file. For example, the kinetics was clarified to fit zero-order reaction with original data and fitting process shown. The state of HNO_3 on TiO_2, the role of HCHO in the renoxification process was elucidated, along with the meanings of the manuscript being stressed as well.

Please see the point-by-point response, the revised manuscript and the revised supporting information for the details. Thanks a lot for your time and help.

Yours sincerely,

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1. The authors stated that "DRIFTS measurements were made to test their homogeneity". The particles were laid and aggregated on the holder in DRIFTS experiment, not the real particles suspended by sprayed into the chamber. I suggested the authors to collect the particles from the chamber to do SEM or TEM, which can give the clear composition of the suspended particles in the chamber, to see whether the particle is physical mixing or chemical dopped.

Response:

DRIFTS is a kind of instrument which can measure the composition of materials. The observed proportional increase of nitrate peak areas in the TiO_2-nitrate composite samples shown in Figure S2 is a good evidence that the prepared samples are homogeneously mixed. Many researches focusing on "renoxification effects" applied similar preparation method as ours to get composite particles (Ndour et al., Geophys. Res. Lett., 2009, 36, L05816; Monge et al., Phys. Chem. Chem. Phys., 2010, 12, 8991-8998), including the article (Ma et al., EST, 2021, 55, 8604) mentioned by the reviewer in his last comment letter. Spectral technique was used to examine the composition of the composite samples. For example, Ma et. al applied micro-Raman spectrometry to confirm that "the form of nitrate was kept during the sample preparation process" (Ma et al., EST, 2021, 55, 8604).

We collected the particles from the chamber to conduct TEM characterization as suggested by the reviewer. Figure 1 displays the TEM and HRTEM images of the TiO_2 and 4 wt.% KNO_3-TiO_2 samples. It can be seen that with small amount of nitrate doping the morphology of the two samples is similar. The lattice-fringe distance of 0.352 nm in TiO_2 sample, and the additional lattice-fringe distance of 0.246 nm in KNO_3-TiO_2 sample, can be ascribed to the interplanar spacing of (101) lattice plane of anatase TiO_2 (Zhang et al., Appl. Catal. B, 2013, 142, 249-258) and (111) lattice plane of TiN (Ma et al., Energy Storage Mater., 2022, 44, 180-189), respectively. This suggests that there is chemical bond formed in the KNO_3-TiO_2 sample. In addition, the obvious enhancement of NOx release in "KNO_3-TiO_2 + HCHO" (corresponds to 110 ppb at 120 min in Figure 2) system compared to "TiO_2 + HCHO" system (3 ppb at 120 min in Figure S5) also indicates that KNO_3 and TiO_2 make the effects together
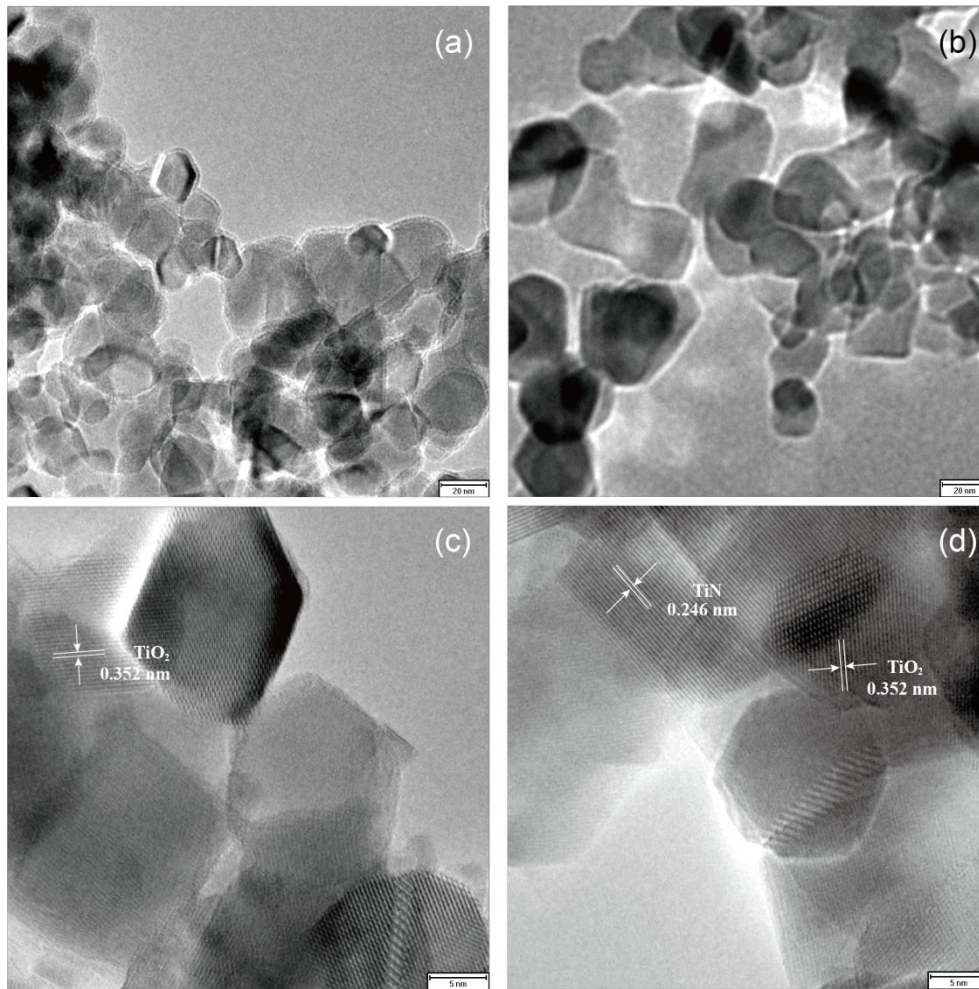
in the chamber.

Figure 1. TEM and HRTEM images of TiO_2 (a, c) and 4 wt.% KNO_3-TiO_2 (b, d) samples.

2. The quantity and the wall loss of particles still have large uncertainty, and this defect wasn't well solved. The size of those symbols in Figure 3-5 is too large to clearly see the difference of particle size distribution at different time. Why did the authors not put all the plots in one figure? I feel that these three figures have some differences. The particle number is very important for the quantification and kinetics study, but we can see "about" in front of most particle numbers description. As I pointed before, large wall loss of particles must exist after the particles sprayed in the chamber. The value of 75mg/250L particles were injected into the chamber, only 8000 particle/cm3 (dN/dLog(dp)) or 4000 particle/cm3 were detected for the most abundant diameter particle, where were the other particles? were they still in the chamber?

Heterogeneous reactions can also occur on the wall! Larger particle can easily deposit on the wall, which also can be found from the difference of the particle distributions between 0 min and hundreds of minutes later in Figure 3-5. Besides, the detected particle size was only up to 250 nm, how about those larger particles? These results were not enough to predict the wall effect.

Response：

    We redrew the size distribution of 4 wt.% KNO_3-TiO_2 and TiO_2 and plotted them together with suitable symbols size, as suggested by the reviewer. It can be seen in Figure 2 that the size distributions of KNO_3-TiO_2 and TiO_2 samples are similar, with both reach stable after about 60 min. The peak number concentration is averaged of 3991 and 3886 particle/cm^{-3} during illumination period for KNO_3-TiO_2 and TiO_2 sample, respectively, indicating that the repeatability of the introduction of particles into the chamber is good and the comparison among different samples in our study is reliable. This can be attributed to the strict cleaning of the chamber and the same operation of each batch experiment. In the new revised supplement, we used this Figure 3 to replace Figure S3, and the description was added in the new revised manuscript in section 2.3.

    The number concentration at different illumination time of each sample is in a range, so we used the word "about" in the response file. We averaged the number concentration after illumination with the value showing above. As for the size of the particles, the SNPS-20 we used can only detect the size distribution range of 7~820 nm, so there is no data about larger particles. However, we can deduce the particle size based on the TiO_2 powder we used. It is a commercial product with particle size of 10-40 nm. So the size of TiO_2 and NO_3^--TiO_2 samples would not become larger than micrometer in the chamber. This can also be confirmed by the TEM images shown in Figure 1 above with both NO_3^--TiO_2 and TiO_2 particles collected from the chamber having size around 15 nm.

    It is true that there is wall loss of particles in the chamber and the deposited particles are still in the chamber. We mentioned this in the original as well as revised manuscript in section 2.3: "*the particle number concentration of KNO₃-TiO₂ or TiO₂*

sample decreased rapidly owing to wall effect including the possible electrostatic adsorption of the particles by the environmental chamber". The wall effect cannot be avoided in the chamber experiments and we had conducted series of comparative experiments including with or without HCHO, with or without TiO_2, with or without illumination, and lamp with or without visible light etc to highlight the positive effect of formaldehyde on the release of NO_x. Moreover, it is a batch experiment as stressed in the manuscript and strict cleaning and operation were conducted to ensure the repeatability, which can also be reflected by the good control of our blank data (Figures S5, S6 and S9).
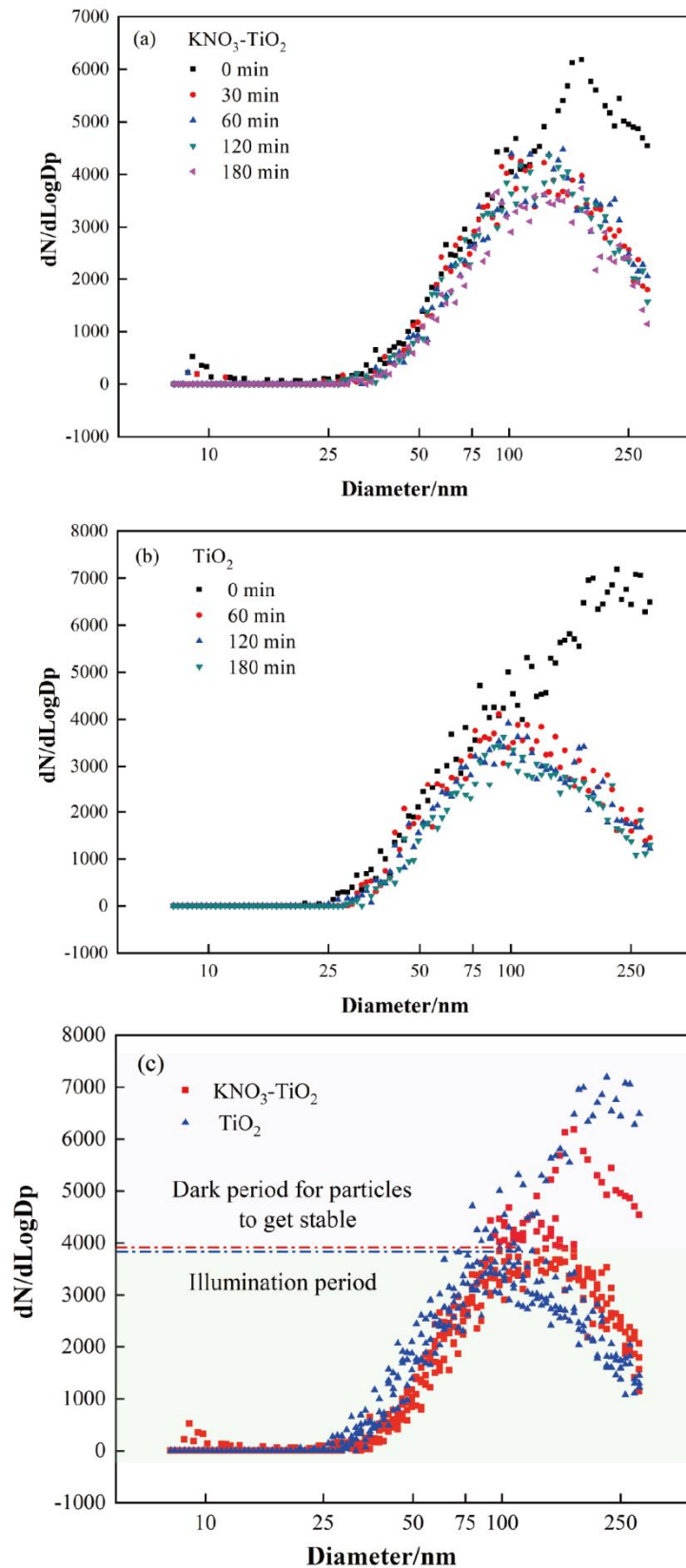
Figure 2. Particle size distribution of 4 wt.% KNO_3-TiO_2 (a), TiO_2 (b) and comparison of 4 wt.% KNO_3-TiO_2 (red line) and TiO_2 (blue line) (c) in environmental chamber with time. (60 minute is the time of turning on the lamps)

3. The proposed mechanisms still couldn't convince me. What's the main significance of this article? The quantity of NOx has great uncertainties, and most of the mechanisms were deduced from so many hypotheses. Though some phenomena and products were observed and detected in previous studies, those proposed key intermediates and products were not directly measured in your experiment. If all those phenomena could be deduced and expected from previous studies, there is no need to do such experiments.

Some supplementary experiments are needed, not in the future but in the present work!

Response：

Here, we would like to stress the background, research design and significance of our work, as have been described in the manuscript. The active nitrogen species (HONO and NOx) have important impacts on the atmospheric oxidative capacity and the transformation of many atmospheric species. Nitric acid and nitrate (HNO_3/NO_3^-) are not only the final sinks of NOx in the atmosphere, but also one of its important sources. The "renoxification" process of NOx generation from NO_3^- is easily overlooked. A fast photochemical renoxification rate of adsorbed HNO_3/NO_3^- to active nitrogen species was detected on real urban $PM_{2.5}$ (EST, 2020, 54, 3121-3128). Ninneman et al (ACS Earth Space Chem., 2020, 4, 1985-1992) found that the "renoxification" of nitrate to NOx is an important source of NOx in rural New York in winter, especially at low O_3 production rates. The transport, transformation, and lifetime of NOx are key factors affecting regional air quality, so the study of the "renoxification" process is of great environmental importance.

In previous studies of the "renoxification" process, it was generally believed that NOx was generated from NO_3^- photolysis ($\lambda \leqslant 350$ nm). Mineral dust mixing with nitrate is ubiquitous in the atmosphere. Our study found that there is a new NOx generation pathway in the coexistence of TiO_2, nitrate and HCHO, with HCHO behaving as a proton-donor. We divide the "renoxification" process of nitrate on the surface of TiO_2 particles into "photolysis renoxification" and "photocatalytic renoxification", which can more clearly understand the promoting effect of TiO_2

photocatalytic performance on the "renoxification" process. Different from the traditional "photolysis renoxification" (caused by NO_3^- photolysis), "photocatalytic renoxification" refers to the "renoxification" process involving h^+ and NO_3 radicals based on the photocatalytic properties of TiO_2.

In this study, the direct photolysis of NO_3^- was excluded, and the "renoxification" of NO_3^- due to the photocatalytic properties of TiO_2, i.e. "photocatalytic renoxification", was investigated separately by monitoring the irradiated wavelength. The role played by HCHO on NOx generation companied with TiO_2's photocatalytic performance was investigated for the first time. The introduction of HCHO is a break from the traditional way of studying atmospheric reactive nitrogen cycle and transformation, and makes it go forward to the real atmospheric situation where multiple pollutants exist simultaneously. The large increase in the release of NOx would have some effects on the formation of important atmospheric oxidants such as OH radicals and O_3. The results of this study will help for assessing the importance of "photocatalytic renoxification" process on atmospheric NOx concentration with the presence of volatile organic pollutants.

The promotion of "photocatalytic renoxification" of NO_3^--TiO_2 particles by HCHO observed in our study cannot be predicted from the previous references. We conducted systematic chamber simulation experiments and obtained the conclusions based on so many comparative experiments and references analyses. NO_3 radical has been proposed to generate in the nitrate-TiO_2 reaction system, but was not detected directly, in many researches (Ndour et al., Geophys. Res. Lett., 2009, 36, No. L05816; Rubasinghege et al., J. Phys. Chem. Lett., 2010, 1, 1729-1737; Chen et al., Chem. Rev., 2012, 112, 5919-5948; Gankanda et al., J. Phys. Chem. C, 2014, 118, 29117-29125; George et al., Chem. Rev., 2015, 115, 4218-4225; Ma et al., EST, 2021, 55, 8604) and may participate in the oxidation of volatile organic compounds (Stockwell et al., J. Geophys. Res.-Oceans, 1983, 88, 6673-6682; Wayne et al., Atmos. Environ., 1991, 25, 1-203; Atkinson et al., Atmos. Environ., 2003, 27, 197-219; Shen et al., EST, 2021, 55, 15658-15671). It is an ideal situation that the supposed intermediates or radicals can be detected in the experimental studies. By using ESR

and chemical probe methods, we can accomplish the detection of some radicals such as OH radical, as has been shown in Figure S10. With the development of more dedicated and portable instruments exploited, more radicals are being expected to be detected easily to support the mechanisms analyses and the field observation results as well.

4. The zero-order reaction kinetics still not right. The y-axis is wrong for the first-order reaction. I feel that the correlation is better in red line than black line in Figure 10. why did the R2 shows opposite results? I still can't accept the zero-order reaction kinetics, the red dots are still not in a line but a curve line with little difference from a line. The authors misunderstand my points, I mean the "60 min for HCHO equilibrium after particles injection" are maintained too long time, that a lot of HCHO (3 ppm HCHO as shown in Figure 12) will be adsorbed on the particles. Then two aspect effects will appear, the first is that HCHO occupy the active sites of particles which inhibit the photoreactions, the other is that both the adsorbed HCHO and gas-phase HCHO can attend the photoreactions. These effects lead the results of Figure 11. The authors should carefully consider the kinetic analysis part, in case mislead the readers.

Response：

The reaction indeed fits zero-order kinetics, not the first-order as the reviewer said. Table 1 shows the raw data of the HCHO concentrations as well as the logarithm (ln) of the concentration over time in TiO_2 and 4 wt.% KNO_3-TiO_2 reaction systems. The curves based on the data were shown in Figure 3. We are sorry that we forgot to exhibit the lnC as the right y-axis in our last response file, and make the reviewer misunderstand. It can be seen that the C-t curve owns better correlation coefficient (R^2) than that of lnC-t curve for both TiO_2 and KNO_3-TiO_2 reaction system, indicating that the reaction fits zero-order kinetics better. In response to the reviewer's feeling of red line having a better correlation than black line, this is because the values become smaller after taking ln, resulting in less difference between the data and therefore appearing more linear. However, the correlation should be judged by correlation

coefficients. Therefore, the zero-order reaction kinetics is right and the kinetic analysis part of the text is correct.

Table1. The raw data of HCHO concentrations over time for TiO_2 and 4 wt.% KNO_3-TiO_2 particles.

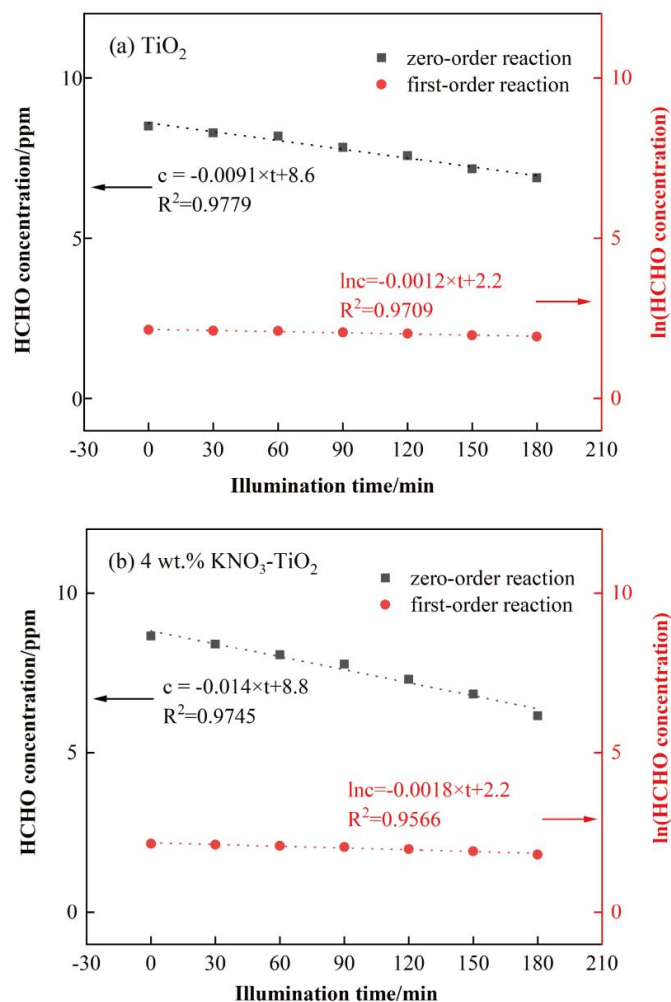| Time (min)	HCHO + TiO$_2$		HCHO + 4 wt.% KNO$_3$-TiO$_2$	
	HCHO concentration (ppm)	ln(HCHO concentration)	HCHO concentration (ppm)	ln(HCHO concentration)
0	8.49398	2.13936	8.65642	2.15830
30	8.28188	2.11407	8.40190	2.12846
60	8.18289	2.10205	8.06253	2.08723
90	7.82938	2.05788	7.76558	2.04970
120	7.57486	2.02483	7.29895	1.98773
150	7.16479	1.96918	6.83232	1.92166
180	6.88199	1.92891	6.15358	1.81703

Figure 3. The comparison of correlation coefficients of zero- and first-order reaction curves. The reaction systems are "HCHO + TiO_2" (a) and "HCHO + 4 wt.% KNO_3-TiO_2" (b), both under 365 nm LED lamps at 293 K and 0.8% of relative humidity.

Concerning the HCHO adsorption as the reviewer mentioned, it is the first step of gaseous species for occurring its heterogeneous reaction on the surface of particles. It needs 60 min for HCHO to reach adsorption saturation as shown in Figure S4. The oxidation process of HCHO has been described in detail in our previous published paper (Scientific Reports, 2017, 7, 10.1038/s41598-017-01396-x). It can be seen from Figure 4 below (Figure 1 in the published paper) that HCHO occurred its oxidation during the reaction with formic acid and CO_2 as the intermediate and final product, respectively. The total carbon involving HCHO, CO_2 and formic acid was near stable throughout the experiments (Figure 4 (d)), implying that the mass balance of carbon was almost closed. This indicates that adsorbed HCHO at this concentration level does not inhibit the reactive sites of the particles, while can be degraded gradually. The effect of HCHO concentration on the renoxification had been discussed in section 3.3.3 in the revised manuscript. Decreased HCHO concentration brought out lower NOx release, which in turn proved the positive effect of HCHO.
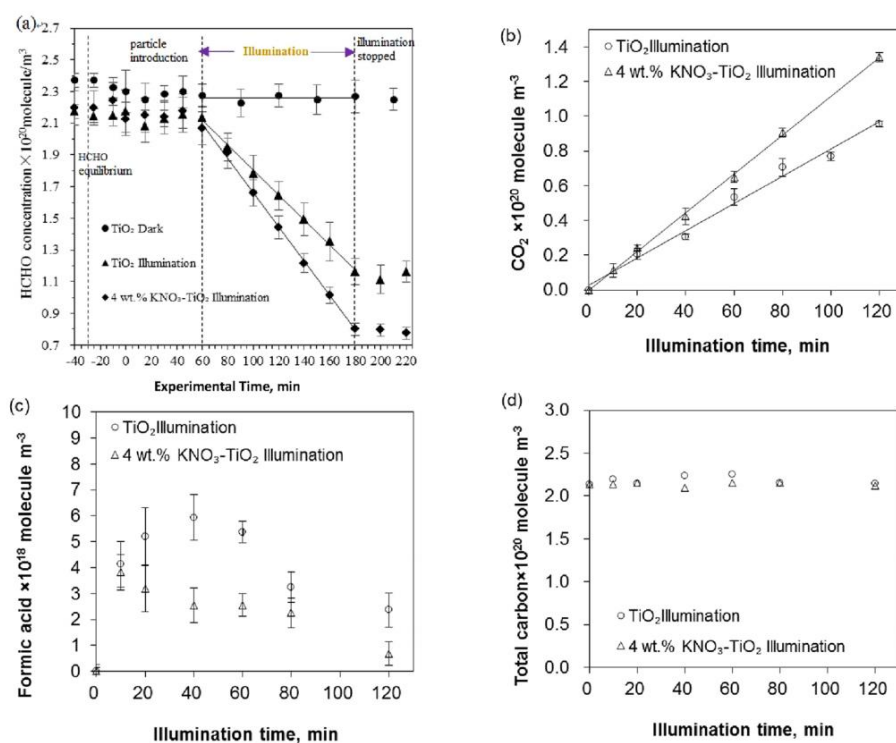

Figure 4. Kinetic curves of reactant and products. (a) Concentrations of formaldehyde. (b) Concentrations of CO_2. (c) Concentrations of formic acid. (d) Concentrations of total carbon (cited from Scientific Reports, 2017, 7, 10.1038/s41598-017-01396-x)

5. The authors misunderstand my question about the mixture of HNO₃ and TiO₂. HNO₃ has small affect on TiO₂, but this treatment has great impact on HNO₃. The mixture can't be HNO₃-TiO₂. What's the state of HNO₃ on TiO₂ surface? gas adsorbed? nitrate? liquid? definitely not HNO₃ solid!!!

Response：

The preparation process of 4 wt.% HNO₃-TiO₂ composite particles is to mix TiO₂ with diluted nitric acid solution, followed by stirring, air-drying, and grinding, as described in the experimental section. The surface presence state of HNO₃ in composite particles were thought in the form of adsorbed HNO₃ and particle nitrate at the same time. As we have elaborated in the last revised manuscript of Line 294-296: "*This is because that HNO₃ dissociates on particle surfaces to generate NO₃⁻, such that HNO₃ exists on TiO₂ as both HNO₃(ads) and NO₃⁻(ads).*"

Other studies have reached similar conclusions, for example, Goodman et. al (J. Phys. Chem. A, 2001, 105, 6443-6457) and Gankanda et.al (J. Phys. Chem. C, 2014, 118, 29117-29125) have demonstrated by FTIR that the interaction of HNO₃ with TiO₂ can be described by the equation (1). In this reaction, HNO₃ reacts with the hydroxyl groups on the TiO₂ surface to form adsorbed nitrate and water molecules.

$$HNO_3 + M(OH) \rightarrow MNO_3(ads) + H_2O(ads) \ (1)$$

(M stands for titanium surface atoms)

On the other hand, Ti-OH in TiO₂ is not enough alkaline to eliminate H⁺ in HNO₃. Furthermore, the photogenerated hole can react with adsorbed water on the surface of TiO₂ under illumination, with the resulting H⁺ enhances the surface acidity. So it is partly in form of adsorbed HNO₃ as well on the surface.

There has been many studies that conducted in laboratory and field observation (Environ. Sci. Technol. 2016, 50, 3530; Environ. Sci. Technol. 2017, 51, 6849; Nat. Geosci. 2011, 4, 440; Environ. Sci. Technol. 2013, 47, 815; ACS Earth Space Chem. 2019, 3, 811) found that the photolysis of surface-adsorbed HNO₃ or particle nitrate enhanced a lot compared to gas-phase HNO₃ photolysis and could be a reactive nitrogen species (NO$_x$ and HONO) source. It is thought that in the presence of protons, the adsorbed NO₃⁻ can interact with protons by H-bonding and electrostatic force.

Because HNO_3 has a stronger oxidation ability than NO_3^-, the reduction of the formed HNO_3 to NOx or HONO is much more thermodynamically favorable (Environ. Sci. Technol. 2020, 54, 3121). The fact observed in our study of significant NOx release when using HNO_3-TiO_2 particle is consistent with the previous studies, and the enhanced NOx release in the presence of HCHO was highlighted with its role being as a proton donor. Focusing on this, this manuscript presents a new pathway of renoxification on photoactive mineral dust and raises the issue of possible effect of atmospheric volatile organic compounds on this process.

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