Response to the reviewer 1's comments:

Referee #1: General Evaluation

This manuscript investigated the effect of HCHO on the photocatalytic renoxification of nitrate on TiO_2 *particles. The investigated system is interesting. However, the experimental design has so many defects. More experiments and verification are needed to support the conclusion.*

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

Comments on Preprint acp-2022-6:

Major comments:

1.Methods: Line 103: 400 L chamber is usually not enough for the investigation of heterogeneous reactions. Besides, only 250 L air was injected into it, which would increase the wall effect of chamber. Line 105-106: How did the author control the chamber temperature? It is well known that the chamber temperature will increase when turn on the lights. Line 111-112: the light intensities for the tube and LED lamp were different, so how to compare their results? Why was only the results in 3.1 obtained under the irradiation of tube lamps? What was the meaning for introducing two kinds of lamps in the smog chamber?

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

(1)Line 103: 400 L chamber is usually not enough for the investigation of heterogeneous reactions. Besides, only 250 L air was injected into it, which would increase the wall effect of chamber.

Response:

The environmental chamber can be used to assess and predict the formation of secondary pollutants. Large volume chamber is helpful for obtaining chemical transformation laws closer to the real atmosphere, although small volume chambers are still used in laboratory dynamics simulation studies due to their economic and flexible features. For example, Shi et al (EST, 2021, 55: 854-861) studied renoxification of suspended submicron particulate sodium and ammonium nitrate through controlled laboratory photolysis experiments using an 150 L Teflon environmental chamber. The reaction system is very similar as ours, focusing on NO_x release from particulate inorganic nitrate with well-characterized light conditions. Another example is Jia et al (Aerosol Sci. Tech., 2014, 48: 1-12), who studied the formation of ozone and secondary organic aerosol (SOA) from benzene–NO_x and ethylbenzene–NO_x irradiations in a 350 L Teflon chamber. The major substances in SOA were determined to be carboxylic acids and glyoxal hydrates. And it was found that the aqueous radical reactions and the hydration from glyoxal can be enhanced under high RH conditions, which can irreversibly enhance the formation of SOA from both benzene and ethylbenzene. In another research, a 151 L chamber was used to study the kinetic of ozone decomposition on luminescent oxide surfaces (Chen et al., J. Phys. Chem. A, 2011, 115: 11979-1198). It is also a simulation research about heterogeneous photochemistry of ozone over mineral dust aerosol, including α-Fe_2O_3, TiO_2, and α-Al_2O_3. The rate and extent of ozone decomposition on these oxide surfaces are found to be a function of the nature of the surface as well as the presence of light and relative humidity, with TiO_2 is active toward O_3 decomposition upon irradiation. Therefore, it is true that 400 L chamber is not so big but can in some extent reflect the simulation results of heterogeneous reaction.

We tried our best to decrease the effects of “wall effect” on the experiment results by two ways. One was to conduct the experiments when the particle size distribution got stable, that is, 60 min after the injection of the particles. As can be seen in Fig S2 of the original manuscript, the size distribution gets stable after 30 min and can sustain for several hours. As stated in text line 166-168 of the original manuscript: "*After the concentrations of both HCHO and aerosol became stable, the lamps were turned on and the concentrations of NOx were monitored.*" Another way was that we strictly carried out blank experiments and all data in the study were subtracted from the corresponding blank data to ensure the reliability. For example, to determine the background value of NO_x in the reaction system, four blank experiments were carried out under illumination without nitrate: "synthetic air", "synthetic air + TiO_2", "synthetic air + HCHO" and "synthetic air + HCHO + TiO_2". In the blank experiments of "synthetic air" and "synthetic air + TiO_2", the NO_x concentration remained stable during 180 min illumination, and the concentration change was no more than 0.5 ppb (Figure S4a of the original manuscript). Therefore, the environmental chamber was thought to be relatively clean, and there was no generation and accumulation of NO_x under illumination. In addition, the chamber was cleaned after each experiment and the repeatability was ensured. To make it clear, we added one sentence to the section 2.3 of the revised manuscript: "For the chamber operation, we completely evacuated the chamber after every experiment, then cleaned the chamber walls with deionized water and then dried by flushing the chamber with ultra-zero air to remove any particles or gases collected on the chamber walls."

Overall, our experiments were conducted under relatively stable conditions, thus to exclude the effects of "wall effect" and the data were reliable.

(2)Line 105-106: How did the author control the chamber temperature? It is well known that the chamber temperature will increase when turn on the lights.

Response:

As stated in line 108-111 of the original manuscript: "*One is a set of tube lamps with a main spectrum of 320-400 nm and a small amount of 480-600 nm visible light (Figure S1a). The other is a set of Light-emitting diode (LED) lamps with a narrow main spectrum of 350-390 nm (Figure S1b)*", the light sources we used emit no infrared lights, and in case 36 W and 3 W of the tube and LED lamps were used, the temperature in the chamber is not easy to be heated. Figure S1b were shown below (Figure 1 here) with the wavelength distribution. We added watt values of the lamps in the section 2.1 of the revised manuscript and above sentence is now as follows:

"*One is a set of 36 W tube lamps with a main spectrum of 320-400 nm and a small amount of 480-600 nm visible light (Figure S1a). The other is a set of 12 W Light-emitting diode (LED) lamps with a narrow main spectrum of 350-390 nm (Figure S1b)*". In addition, we controlled the temperature of the room where the chamber is, keeping it at 20 degrees all the time. So we consider the effect of temperature to be negligible in this study.

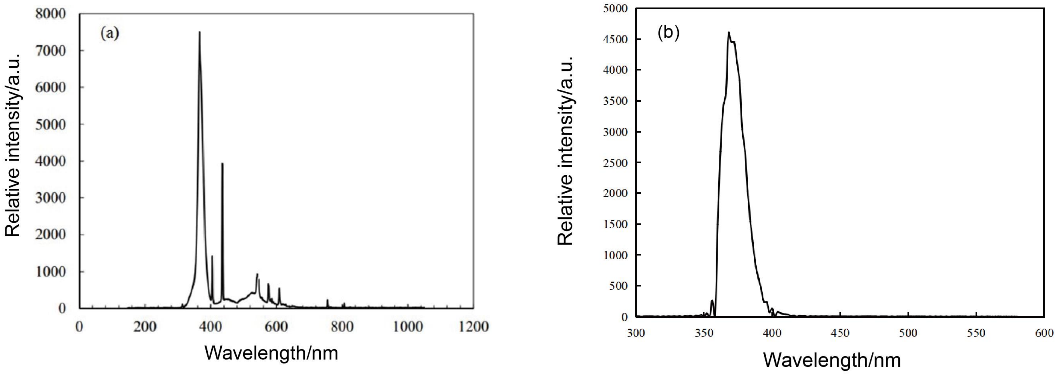

Figure 1. Spectral energy distribution of (a) 365 nm tube lamps and (b) 365 nm LED lamps.

(3)Line 111-112: the light intensities for the tube and LED lamp were different, so how to compare their results? Why was only the results in 3.1 obtained under the irradiation of tube lamps? What was the meaning for introducing two kinds of lamps in the smog chamber?

Response:

The reaction systems and aims of the two kinds of light sources were different, which were summarized in the following Table 1. The results of tube lamp and LED lamp would not be compared, but had their own purpose, individually.

For tube lamp (contains both ultraviolet and visible light) system in section 3.1, there is no HCHO but only nitrate with or without TiO_2 (KNO_3-SiO_2 or KNO_3-TiO_2/SiO_2). The aim is to prove that NO_3 radical can be produced via the reaction between excited TiO_2 and nitrate, with its photolysis under visible light producing NO_x.

For LED lamp (contains only ultraviolet) system in section 3.2, HCHO was introduced and the particles are KNO_3-TiO_2 or HNO_3-TiO_2. The aim is to avoid the photolysis of NO_3 radicals under visible light, but to see if the produced NO_3 radicals can be reacted with HCHO. As stated in line 226-229 of the original manuscript: "*Therefore, the LED lamp setup was used in subsequent experiments to exclude the direct photolysis of both KNO_3 and $NO_3\cdot$, but allow the excitation of TiO_2. This approach allowed us to investigate the process of photocatalytic renoxification caused by HCHO in the presence of photogenerated $NO_3\cdot$.*" In this way, the formation of NO_x can be attributed to the photolysis of HNO_3, coming from the possible hydrogen-abstraction reaction of HCHO with NO_3 radicals, as discussed in the later part of section 3.2.

Therefore, the design of our experiments is: (1) Section 3.1 using tube lamp to prove that NO_x is not coming from KNO_3 UV-light photolysis, but from the visible-light photolysis of NO_3 radical. By this way to prove the photocatalytic effect of TiO_2 on "renoxification" process, that is "photocatalytic renoxification"; (2) Section 3.2 using LED lamp to ensure no photolysis of both KNO_3 and NO_3 radical, and in this case to investigate the effect of HCHO on the release of NO_x in the presence of NO_3 radical, i.e., the effect of HCHO on the "photocatalytic renoxification". In order to make the readers understand clearer, we rewrote the abstract according to this logic and defined the term "photocatalytic renoxification".

Table 1. A comparison of the two light sources used.

Light source and Wavelength range	Section	System	Phenomenon	Contents/Implications
TUBE LAMP, 320-400 nm with small amount of 480-600 nm	3.1	4 wt.% KNO_3-SiO_2 (NO HCHO)	No NOx was released	320-400 nm irradiation cannot make nitrate photolyze, so to exclude the photolysis source of NOx from nitrate. [Fig 1]
		4 wt.% KNO_3-TiO_2 (1 wt.%)/SiO_2 (NO HCHO)	NOx release was observed	TiO_2 was composited to SiO_2, to see the effect of TiO_2 along with nitrate. 320-400 nm irradiation can excite TiO_2 to generate electron-hole pairs. Nitrate can react with photogenerated holes to produce NO_3 radicals 480-600 nm irradiation can make NO_3 radical photolyze, generating NOx Above explanation can be seen in section of 3.1 and the equations 1-4 in the original manuscript.

Section 3.1 proves that NO_3 radical can be produced in the condition of "nitrate+ TiO_2 (excited by the UV light of the tube lamp)", then NO_3 radical undergo photolysis (under visible light of the tube lamp) to produce NOx. In order to avoid the photolysis of NO_3 under visible light, no tube light containing visible light was used any more in section 3.2. The aim of 3.2 is to investigate whether the produced NO_3 radical can be captured by HCHO. This explanation can be seen in the first paragraph in section 3.2, that is Line 219-229 of the original manuscript.				
LED LAMP, 350-390 nm	3.2	(WITH HCHO) 4 wt.% nitrate-TiO_2	NOx release was observed	350-390 nm irradiation cannot make nitrate photolyze, so to exclude the photolysis source of NOx from nitrate. [Fig S5] 350-390 nm irradiation can excite TiO_2 to generate electron-hole pairs, so as to generate NO_3 radical. 350-390 nm irradiation cannot make NO_3 radical photolyze. NO_3 radical can react with HCHO to produce HNO_3(ads) The observed NOx comes from the photolysis of HNO_3(ads).
This explanation can be seen in section 3.2, including Fig 2 and equations 5-8.				

2.Important defect of this article is the composition of the mixture in the part of "2.2 nitrate-TiO_2 composite samples": "TiO_2 was simply mixed in nitrate solutions at the desired mass mixing ratio to obtain a mash. The mash was dried at 90℃ and then ground carefully to ensure a uniform composite of particles." How did the author ensure that the particles are uniform composite of nitrate and TiO_2? Did the author do some experiments to confirm these? For example, in the reference of Ma et al (EST, 8604-8612, 2021), the nitrate and TiO_2 mixture was dripped onto a quartz tube inner all, then images and Raman spectra of single composition and mixture were analyzed, and mixture were confirmed to form. However, in this work, the generation method of mixture particles is different from that of Ma's work, and these mixture particles are sprayed by synthetic air into PVF bag. No experiments have been given to confirm the composition of the mixture particles in the chamber. In my opinion, this method can't generate a uniform composite of nitrate and TiO_2!!! The composition and the nitrate content are the most important quantitative method factors of all the experiments in the article. If the composition and nitrate content can't be control, how *to compare the NOx concentration in different experiments? Then, all the results are not convincing!!!*

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We prepared the composite particles carefully and ensured its homogeneity. During the preparation of nitrate and TiO_2 composite samples, we used a very small amount of nitrate solvent, which is of 2 mL. With a relatively large specific surface area (~54.28 m^2/g) and a large amount (250 mg) of TiO_2, the mixture was viscous and then quickly dried at 90°C, followed by a thorough grind for 30 min. So, nearly no loss of TiO_2 due to no use of filtration, and nearly no loss of nitrate pyrolysis due to low temperature of drying. Concerning the work of Ma et al (EST, 2021, 8604-8612) mentioned by the reviewer, the nitrate and oxides were mixed by dispersing a total mass of 1.0 g of oxide powder and 0.02 g of nitrate in 50.0 mL of ultrapure water. The measured nitrate loading percent (1.9-2.0 wt%) was very closed to theoretical value (2.0 wt%). This preparation method was very similar to ours in that both TiO_2 powders were dissolved in a nitrate solution. So the composites of nitrate and TiO_2 we obtained by our preparation method are thought to be uniform.

In addition, we used diffuse reflectance fourier transform infrared spectroscopy (DRIFTS) to characterized the structure of the particles, with the results approving the homogeneity. DRIFTS spectra of KNO_3-TiO_2 particles with different contents of nitrate as well as the KNO_3 particle were shown in the following Figure 2. It can be seen that IR spectra of the composited particles with KNO_3 contents higher than 1 wt% were very close to that of KNO_3. According to Aghazadeh's (J Ultrafine Grained Nanostruct Mater, 2016, 49(2): 80-86) and Maeda's (Applied Catalysis B: Environmental, 2011, 103(1-2), 154) work, 1760 cm^{-1} are the vibrating peaks of nitrate. The ratios of the peak area from 1730-1790 cm^{-1} for 1, 4, 32, 80 wt.% composited samples is 1: 4.1: 29.8: 81.6, which is very close to that of theoretical value, proving that the samples were uniformly mixed. This DRIFTS figure has been added as Figure S2 in *Supplement* of the revised manuscript, with its description added in section 2.2 of the revised manuscript.

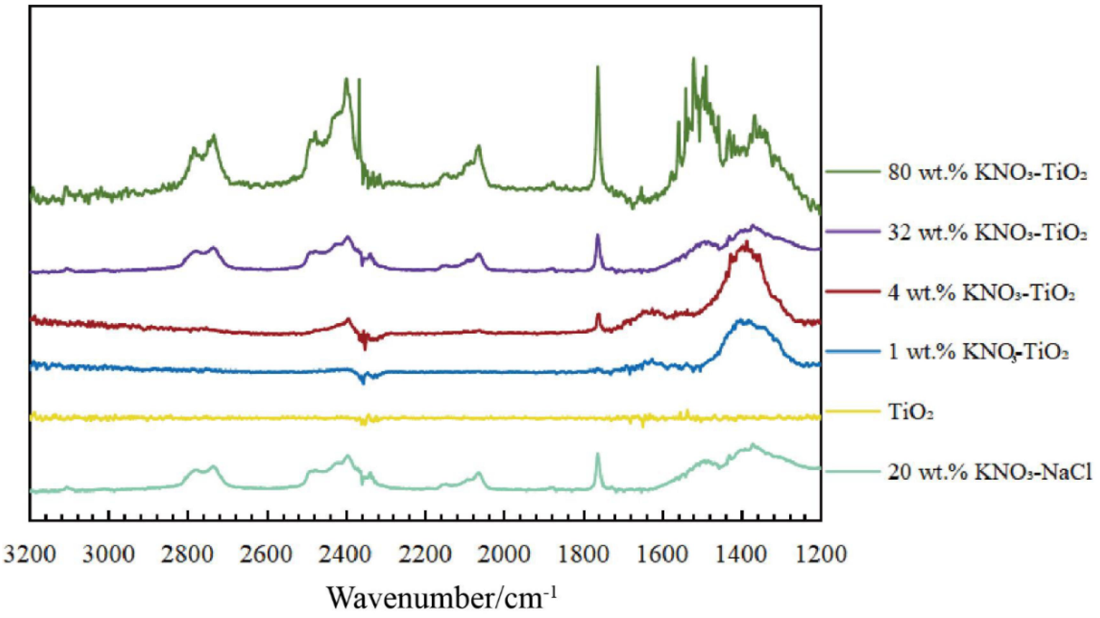

Figure 2. DRIFTS spectra of TiO_2 particles compounded with different mass fractions of KNO_3.

3.Another important defect of this article is the quantitative method of NOx concentration. As shown in Ma's work, they used the normalized concentration (ppb/mg) to quantify NOx. However, this work just used the NOx concentration (ppb) to compare different experiments, which meant that if more reactants were added in the chamber, the generated NOx concentration would be higher. The initial mass concentration of particles was 300 mg/m^3 *(75mg/250L), and the concentration of HCHO was 10 ppm, which were much higher than that in the real environment and resulted in that the obtained results could not be directly used for an analogy to real environment. The results with ppb as unit are meaningless to reflect their influence in the real atmosphere. Were the particles kept the same in different experiments during the reaction? The author mentioned that the wall loss of particle in the smog chamber was very high at the beginning. And the wall loss for different kinds of particles and for the same kind of particles in different experiment (maybe affected by the conditions of the smog chamber wall) should be different. How did the author ensure* *that the particle distributions were the same in different experiments when turned on the light? Besides, the surface area, as an important factor in heterogeneous reactions, has not been detected in the experiments. Different surface areas directly affect the irradiation surface of* TiO_2*, the uptake of HCHO and the release of NOx. The missing information of surface area would result in the large uncertainties in the experiments. At least, the authors should give a normalized NOx concentration, then different experiments can compare with each other and give the reasonable results and reflect the influence in the real environment.*

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

(1)Another important defect of this article is the quantitative method of NOx concentration. As shown in Ma's work, they used the normalized concentration (ppb/mg) to quantify NOx. However, this work just used the NOx concentration (ppb) to compare different experiments, which meant that if more reactants were added in the chamber, the generated NOx concentration would be higher.

Response:

For flow tube experiments, the flow tube was usually weighted before and after its loading with samples and the normalized concentration (ppb/mg) was used for a better comparison between different samples, as what has been done as Ma's work. However, in our experiments, the amount of the different samples sprayed into the chamber is same, so the mass normalization is not necessary. That is, no matter whether it is expressed as ppb/mg or ppb, the same trend will be obtained, which will not affect the conclusions of our study.

(2)The initial mass concentration of particles was 300 mg/m^3 *(75mg/250L), and the concentration of HCHO was 10 ppm, which were much higher than that in the real environment and resulted in that the obtained results could not be directly used for an*

analogy to real environment. The results with ppb as unit are meaningless to reflect their influence in the real atmosphere.

Response:

The value of 75mg/250L is the amount we injected into the chamber, but according to the size distribution measurement, the real suspended particle concentration was not that high. As shown in Figure S2 of the original manuscript, the number concentration of TiO_2 particles is about 8500 particle/cm^{-3} after reaching stability. This level of number concentration was observed by Wang et al (Environ. Chem., 2015, 34(9): 1619-1626) who measured the particle size distribution of atmospheric particulate matter number concentrations in Nanjing in August 2013, with the particle number concentration of about 8000 particle/cm^{-3}. As stated in line 156-158 of the original manuscript: " *The size distribution of TiO_2 reached stable after about 60 min with the peak particle size was about 120 nm, similar to that of atmospheric particles in some urban areas in China (Wang et al., 2015; Li et al., 2019).*" We checked our size distribution data of different samples, and found that the number concentration is not that high and usually around 4000 particle/cm^{-3} when reaching stability, with the figures shown below (Figures 3-5 in this file). So, the Figure S2 in the original manuscript was deleted and replaced by the following Figure 3 (Figure S3 in the revised supplement).

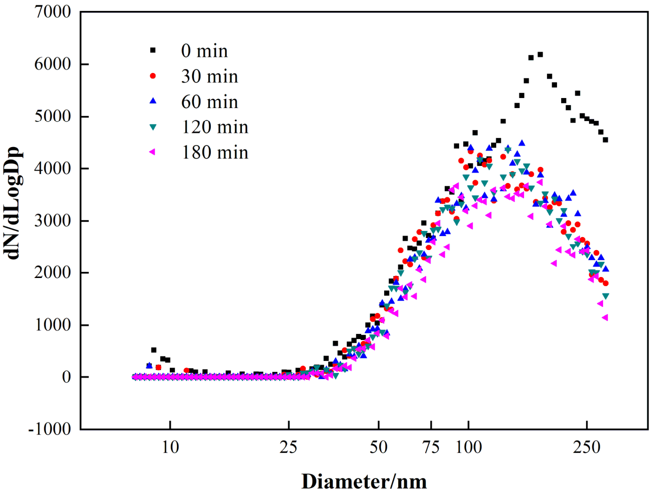

Figure 3. Changes of particle size distribution of 4 wt.% KNO_3-TiO_2 particles in environmental chamber with time.

We admit that 10 ppm of HCHO is too high, so we also performed experiments with low concentrations of HCHO (1 ppm), as described in section 3.3.4 of the manuscript. The positive effect of HCHO on the photocatalytic renoxification of KNO_3-TiO_2 particles was still observed, with NO_2 concentration first increasing and then decreasing (Figure S10 of the original manuscript). Atmospheric formaldehyde concentrations are generally very low. However, in cities with high traffic density, because combustion produces emissions, formaldehyde concentrations will be much higher than normal. In the indoor environment, formaldehyde levels can increase due to smoking, emissions from gas stoves and furniture, and can reach up to around 0.4 ppm (Formaldehyde. In: Wood dust and formaldehyde. Lyon, International Agency for Research on Cancer, 1995, 217-362). So, we assume that the positive effect of HCHO on the renoxification may still exist at some specific situation with its high concentration, which requires further investigation. To make the presentation of our results more accurate, we have added this sentence in the section 4 of the revised manuscript: "*Although in the case of high concentrations of HCHO in our experiment, the response to the real situation will be biased, the results of this study illustrate a possible way of HCHO in influencing nitrate renoxification in the atmosphere.*"

(3)Were the particles kept the same in different experiments during the reaction? The author mentioned that the wall loss of particle in the smog chamber was very high at the beginning. And the wall loss for different kinds of particles and for the same kind of particles in different experiment (maybe affected by the conditions of the smog chamber wall) should be different. How did the author ensure that the particle distributions were the same in different experiments when turned on the light?

Response:

Thanks for the reviewer's thoughtful question. As mentioned before, we deflated and cleaned the chamber for each experiment, and the operation of each experiment was almost identical. So the particle number size distribution of the same kind of particles would be quite same, which can be proved by the following Figures 4 and 5.

The operation sequence of the experiment is as follows: HCHO was introduced firstly, and wait 60 min for its stability; then the particle was introduced instantly, and need 30 min for its stable, and another 30 min for HCHO's second stability; then the lights were opened. The experiment operation has been rewritten in the revised manuscript.

The left picture in the following Figure 4 shows the first 60 min of the size distribution in the dark, and the right picture of the size distribution during the irradiation time. Figure 5 is another batch experiment of TiO_2 in the chamber with the same operation, and it shows very similar size distribution from 0-60 mins and 120-180 mins.

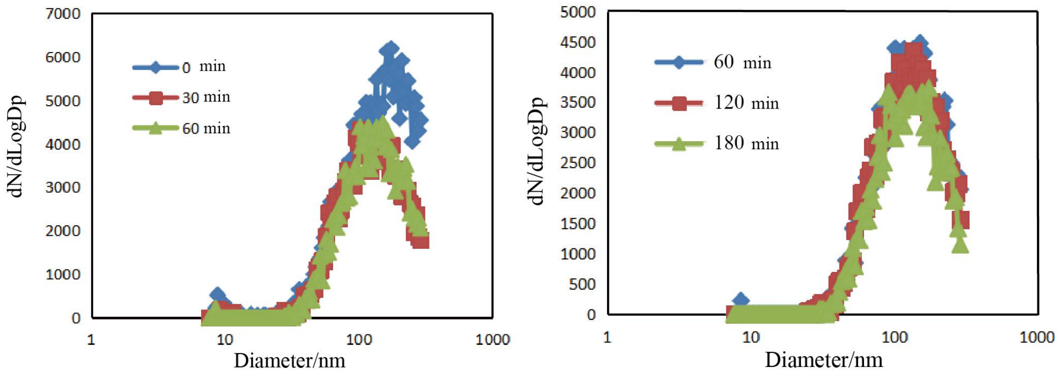

Figure 4. Changes of particle size distribution of TiO_2 particles in environmental chamber with time. Left: Before irradiation; Right: After irradiation.

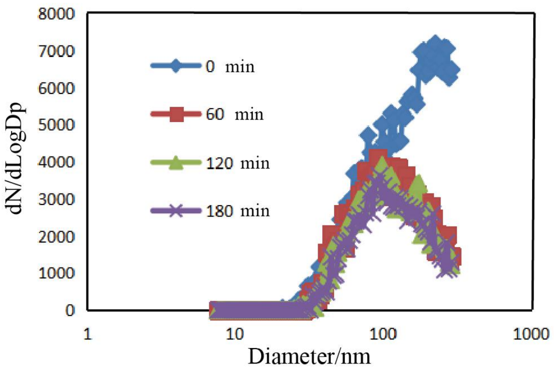

Figure 5. Changes of particle size distribution of TiO_2 particles in environmental chamber with time (Another batch experiment).

As for different kinds of particles, as comparison of Figure 3 with Figures 4 and 5, both main particle size (about 120 nm) and particle number concentration (about 4000 particle/cm^{-3}) are similar. Therefore, the particles can be kept the same in different experiments during the reaction, not only for the same particles but also for different kinds of particles. This is because of the same operation and the similar surface area of different kinds of particles (same loading of nitrate) as will be mentioned below.

(4)Besides, the surface area, as an important factor in heterogeneous reactions, has not been detected in the experiments. Different surface areas directly affect the irradiation surface of TiO_2*, the uptake of HCHO and the release of NOx. The missing information of surface area would result in the large uncertainties in the experiments. At least, the authors should give a normalized NOx concentration, then different experiments can compare with each other and give the reasonable results and reflect the influence in the real environment.*

Response:

We agree with the reviewer that surface area will affect the reaction process. We once measured BET of the KNO_3-TiO_2 particles with the results shown in Table 2. It can be seen that the BET values gradually decrease as the nitrate loading increases. As suggested by the reviewer, the surface area normalized reaction rate should be used to compare the particles. It is a regret that we did not measure the BET of NH_4NO_3-TiO_2 particles, so we cannot get the normalized parameter for NH_4NO_3-TiO_2 particles. Therefore, for sake of the reliability of the results, we deleted the 3.3.2 section "the influence of nitrate content" of different kinds of nitrate. Except for section 3.3.2, the loadings were all 4 wt.% of nitrate. According to Table 2, the BET surface areas of the particles did not change much at 4 wt.% loading, which were mainly dependent on the specific surface area of the main body of TiO_2. So the estimated difference in BET surface area of TiO_2 loaded with different nitrates at 4 wt.% loading is not significant and has little effect on the reaction results.

Table 2. BET surface area of composite particles with different KNO_3 content.

KNO_3 content in composite particles wt.%	BET m^2/g
0	54.28
1	50.7
4	48.04
12	41.77
20	36.86
32	26.67
50	18.45
80	5.61

4.Gas HCHO and mixture particles of TiO_2 and nitrate were contained in the system. Although some controlled experiments were conducted, the role of TiO_2 and HCHO still could not be isolated. A series of important experiments such as HCHO and single nitrate particles under irradiations are needed.

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We agree with the reviewer that controlled experiments are needed not only for “TiO_2 + HCHO” system, but also for “HCHO+nitrate” system, which have both been conducted in our study. Figure S6 in the original manuscript presented the HCHO decay with irradiated TiO_2, indicating the photocatalytic role of TiO_2. For “HCHO+nitrate” system, because the nitrates in our study were all loaded on particles, we composited nitrate with inert SiO_2. As shown in Figure 6 below, when only KNO_3-SiO_2 was present in the chamber (without HCHO), NO_x concentrations fluctuated within the instrumental measurement error (0.5 ppb) both in the dark and under 365 nm LED illumination. When HCHO occurred in the chamber with KNO_3-SiO_2 particles, no NO_x production was observed in the dark and under 365 nm LED illumination, indicating that HCHO could not be oxidized on the surface of non-photocatalytically active particles. We have added this figure as Figure S9 in the revised supplement with its explanation in section 3.2.

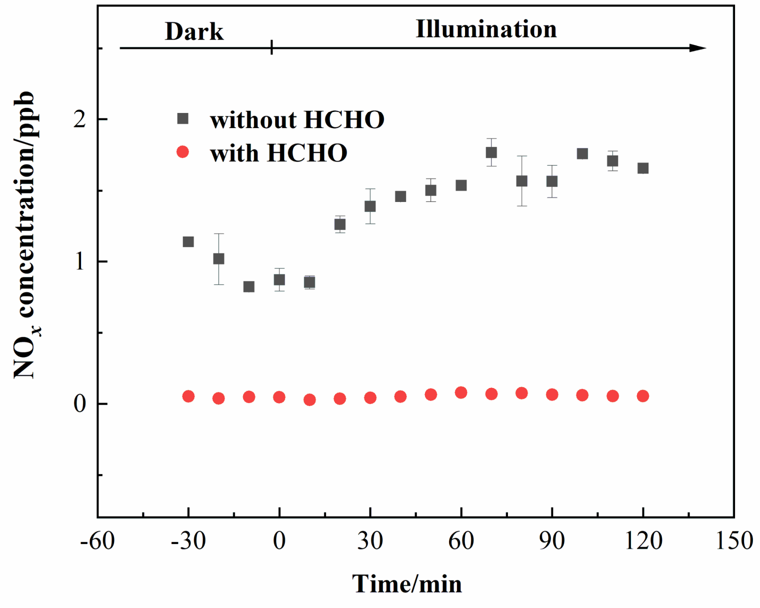

Figure 6. Effect of formaldehyde on the renoxification processes of 4 wt.% KNO_3-SiO_2 particles at 293 K and 0.8% of relative humidity. 365 nm LED lamps were used during the irradiation experiment. The initial concentration of HCHO was about 9 ppm.

5.All the proposed mechanisms couldn't be well supported only by the changes of NOx concentration. This work and Ma's work indicate HONO, HNO_3, NO_3 radical, NOx could form in these reaction systems. However, HONO, HNO_3, NO_3 radical could lead the overestimation of NO_2 concentrations by chemiluminescence method. How did the authors exclude the effect of these species? Besides, most important products such as NO_3, HNO_3, HONO were not detected in the experiments except OH radical. How did the authors make sure that the reaction pathway followed the proposed mechanisms? It is well known that TiO_2 can photocatalysis HCHO, can this reaction affect the formation of NOx?

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

(1)All the proposed mechanisms couldn't be well supported only by the changes of NOx concentration. This work and Ma's work indicate HONO, HNO_3, NO_3 radical, NOx could form in these reaction systems. However, HONO, HNO_3, NO_3 radical could lead the overestimation of NO_2 concentrations by chemiluminescence method. How did the authors exclude the effect of these species? Besides, most important products such as NO_3, HNO_3, HONO were not detected in the experiments except OH radical. How did the authors make sure that the reaction pathway followed the proposed mechanisms?

Response:

It is a regret that we did not detect the formation of HONO, HNO_3 and NO_3 radical due to technique limitation. The effects of these compounds on NOx measurement has been discussed in section 3.2 of the original manuscript. Most of our experiments were conducted in dry condition (0.8% RH), and according to Zhou et al (Geophys. Res. Lett., 2003, 30, 10.1029/2003gl018620), the rate of NO_x generation from HNO_3 photolysis was greater than 97% of the total product at RH=0%. So the formation of HONO in our study was estimated to be very low. For larger RH conditions as discussed in section 3.3.3 of the original manuscript, HONO(ads) can be generated due to the reaction of NO_2 with adsorbed H_2O, which can be desorbed from the surface and released into the gas phase. While according to Shi et al (Environ. Sci. Technol., 55, 854-861,2021), the effect of HONO on NO_x analyzer measurements can be neglected in case of high NO_x concentration in the system. The NO_x concentration in our study in most cases is about 100 ppb, so we think the effect of other products on product distribution and NO_x measurements was negligible

In response to the speculation of HNO_3 production, we measured the pH of water extracts in NO_3^--TiO_2 systems with and without HCHO, and found that pH was greatly reduced in the presence of HCHO (Figure 7 below). The pH decreases by 1.7% and 2.1% for KNO_3-TiO_2 and NH_4NO_3-TiO_2 particles, respectively, suggesting the formation of acidic species such as HNO_3(ads) in this study. We have added this results in the revised manuscript as it appears in the section 3.2: "*Next, we measured the pH of water extracts in NO_3^--TiO_2 systems with and without HCHO. It was found* *that for KNO_3-TiO_2 and NH_4NO_3-TiO_2 particles, the pH decreased by 1.7% and 2.1%, respectively, suggesting the formation of acidic species such as HNO_3(ads) in this study.*"

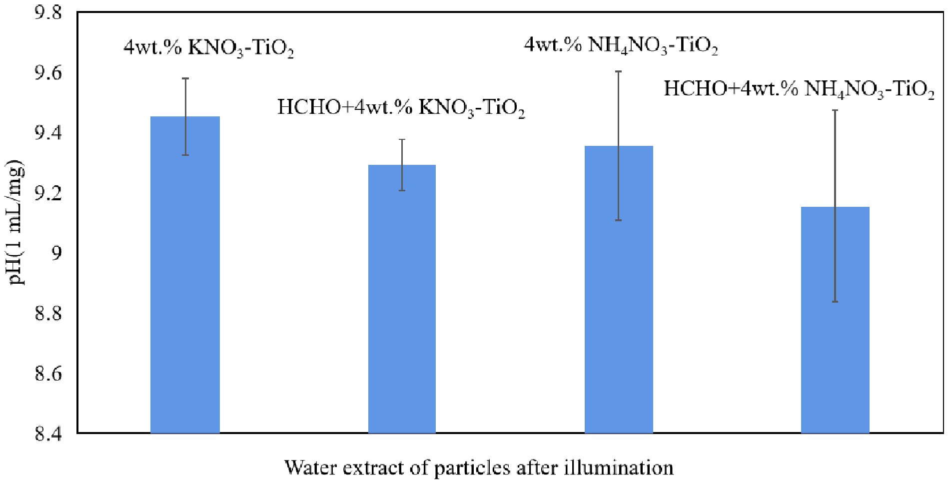

Figure 7. pH values of water extract of KNO_3-TiO_2 and NH_4NO_3-TiO_2 particles in the chamber with or without HCHO under 365 nm LED lamps illumination at 293 K and 0.8% of relative humidity.

The generation of NO_3 radicals can be indirectly proved by the results in section 3.1 and Figure 1 of the original manuscript, as we have responded to comment # 1 (3) and displayed in above Table 1. Another similar example is the published work of our group (Sci. Rep., 2017, 7, 1161). By using the same chamber, the photoreaction rate constants of HCHO on TiO_2 and KNO_3-TiO_2 aerosols under "365 nm lamp" or "365 nm lamp + yellow fluorescence lamp (450–750 nm)" illumination were compared (Figure 8 below). The oxidation rate constants of HCHO over TiO_2 were comparable under these two illumination conditions, due to that TiO_2 is not sensitive to visible light. However, the rate constant on KNO_3-TiO_2 aerosol under illumination of both lamps was lower than that under only the "365 nm lamp", indicating a reduced oxidation rate due to NO_3 radical photolysis by visible light. This provides experimental evidence for the existence of NO_3 radical.

As we have mentioned in the section 3.3.3 of the original manuscript, in the presence of H_2O, in addition to the suggested NO_3^--$NO_3\cdot$-HCHO-HNO_3 pathway, there are a variety of HNO_3 generation paths, such as the hydrolysis of N_2O_5 via the NO_2-N_2O_5-HNO_3 pathway, the oxidation of NO_2 by ·OH, and the reaction of NO_3· with H_2O, all of which require further consideration and study. It is a regret that due to the technique limitations, we did not detect these species directly. We will dedicate to detect these species by some instruments in the future.

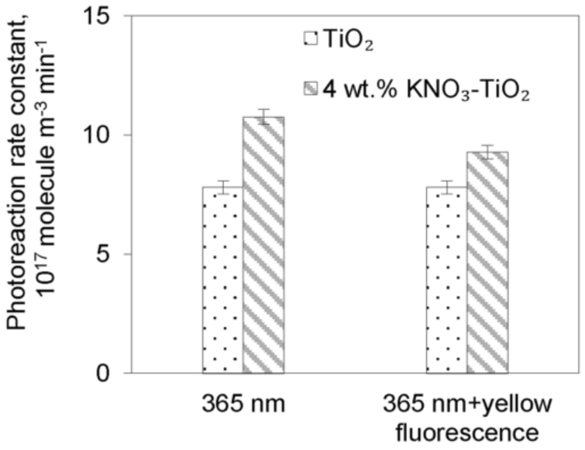

Figure 8. Photoreaction rate constants with light illumination. HCHO photoreaction rate constants on TiO_2 or 4 wt.% KNO_3-TiO_2 aerosol in the condition of 8% RH under light illumination of "365 nm" or "365 nm + yellow fluorescence", respectively. (Sci. Rep., 2017, 7, 1161)

(2)It is well known that TiO_2 can photocatalysis HCHO, can this reaction affect the formation of NOx?

Response:

Yes, HCHO can be degraded in the presence of irradiated TiO_2 and will affect the release of NO_x, which had been discussed in the original manuscript. We observed the decrease of HCHO concentration both in "TiO_2+HCHO" and in "TiO_2/NO_3^- +HCHO" systems. The results were shown in Figure S6 of the original manuscript (Figure 9 here). For better understanding, we revised the last sentence "Future studies should explore whether HCHO affects the photocatalytic renoxification of NO_3^--TiO_2." in the second paragraph of section 3.2 as "In the following study, the effect of HCHO on the photocatalytic renoxification of NO_3^--TiO_2 was explored".

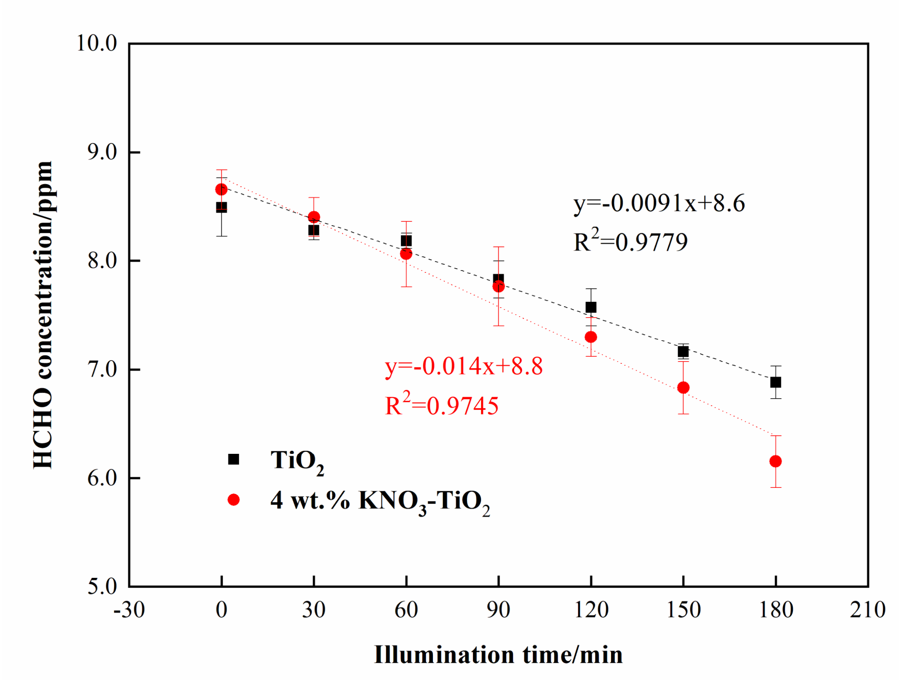

Figure 9. Photocatalytic degradation curve of HCHO on TiO_2 and 4 wt.% KNO_3-TiO_2 particles under 365 nm LED lamps at 293 K and 0.8% of relative humidity.

The decreased concentration of HCHO during this process can affect the formation of NO_x, which can be reflected by the flattening trend of NOx production after 60 min irradiation. This effect had been discussed in the original manuscript, line 247-249: "*The slow stage is due to the photodegradation of HCHO on KNO_3-TiO_2 aerosols, which led to a decrease in its concentration, gradually weakening the positive effect*". In addition, the amount of NO_x was also significantly reduced under the experiment of low concentration of HCHO (section 3.3.4 of the original manuscript), proving again the important role of HCHO in NO_x release.

6.The mixture of HNO_3 and TiO_2 was used to support that HNO_3 was an important intermediate to form NOx. However, this logic is not right. If it is right, then any N-contained components mixed with TiO_2 that enhanced the generation of NOx could be thought as the intermediates of NOx formation. The direct way to identify the intermediates is to measure them such as FTIR/DRIFTS to measure the adsorption products.

Response:

Thanks for your comments, which will be valuable and helpful for revising and improving the manuscript. What we want to emphasize here is that a hydrogen abstraction reaction was occurred between HCHO and NO_3 radical to produce HNO_3, with the description shown in equation 5 and Line 252-254 in the original manuscript (*This burst-like generation of NO_x can be ascribed to the reaction between generated $NO_3\cdot$ and HCHO via hydrogen abstraction to form adsorbed nitric acid ($HNO_3(ads)$) on TiO_2 particles*). That meant the formed HNO_3 came from the original nitrate, and was responsible for the fast NO_x release. The HNO_3-TiO_2 system is used as a comparison test to demonstrate the proposed mechanism and the photolysis contribution of HNO_3 to NO_x. FTIR/DRIFTS can be used for detecting species formation, but what we used in our study were nitrates, so no significant change in peak intensity would be observed.

Minor comments:

1.Abstract: many sentences are confusing me! I can't understand what the main meaning of the work. What's the main results. The languages need to be improved.

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript. In the revised manuscript, we rewrote the abstract for better understanding. The terms of "renoxification" and "photocatalytic renoxification" were stated firstly and then the reaction system was introduced. After that, the experimental results were shown, and the reaction pathway was suggested. The revised abstract is as follows: "Renoxification is the process of recycling of NO_3^-/HNO_3 into NO_x under illumination, which is mostly ascribed to the photolysis of nitrate. TiO_2, a typical mineral dust component, can play its photocatalytic role in "renoxification" process due to NO_3 radical formed, and we define this process as "photocatalytic renoxification". Formaldehyde (HCHO), the most abundant carbonyl compound in the atmosphere, may participate in the renoxification of nitrate-doped TiO_2 particles. In this study, we established an environmental chamber reaction system with the presence of HCHO and nitrate-doped TiO_2. The direct photolyses of both nitrate and NO_3 radical were excluded by adjusting the illumination wavelength, so as to explore the effect of HCHO on the "photocatalytic renoxification". It is found that NO_x concentration can reach up to 110 ppb for 4 wt% KNO_3-TiO_2 particles, and was 2 orders of magnitude higher than in the absence of HCHO. Nitrate type, relative humidity and HCHO concentration were found to influence NO_x release. Adsorbed HCHO may react with nitrate radicals through hydrogen abstraction to form adsorbed HNO_3 on the surface. The mass generation of NO_x was suggested to via the NO_3^--$NO_3\cdot$-HCHO-HNO_3-NO_x pathway, with HCHO and TiO_2 exhibiting a significant synergistic effect. Our proposed reaction mechanism by which HCHO promotes photocatalytic renoxification is helpful for deeply understanding the atmospheric photochemical processes and nitrogen cycling.

2. "photocatalysis", "photolysis", "photocatalytic", "photochemical" appeared in the manuscript everywhere, the author should make sure the exact meaning of these words and give the right usage of these words.

Response:

Thanks for your comments. Table 3 illustrates the use of the four words. "Photocatalysis" and "photocatalytic" are used to refer to the chemical reactions that occur when photocatalysts such as TiO_2 are irradiated. The word "photolysis" refers to the breaking of chemical bonds of the substance itself under light, especially ultraviolet light, when there is no photocatalyst. In the manuscript, "photolysis" refers to the reaction of N-containing species themselves under irradiation. These three can be grouped together as "photochemical reactions". In the manuscript, we use "photochemical" in order to illustrate the broad meaning of such kind of reactions occurred in the atmosphere. For example, "photochemical processes" in the paper refers to atmospheric oxidation and nitrogen cycling. The different words being used to better distinguish the reactions that occur in different situations. We have corrected the inappropriate wording in the revised manuscript, shown also in Table 3 below.

Table 3. Distinction between “photocatalysis”, “photolysis”, “photocatalytic” and “photochemical”.

Word	Meaning	Usage in our study
Photocatalysis (noun)	The photocatalytic properties and photocatalytic activity of the compounds.	This word was used only once in the abstract section. In order to simplify the use of words in the paper, we have modified the abstract so that the word is no longer used.
Photolysis (noun)	The chemical bonds of the substance itself are broken under light, especially ultraviolet light.	“Photolysis” refers to the reaction of N-containing species themselves under irradiation
Photocatalytic (adjective)	Photocatalytic effect of photocatalyst.	The word is used wherever TiO_2 is mentioned.
Photochemical (adjective)	Series of chemical reactions that occurred under irradiation.	Some sentence such as “..photochemical cycle of HOx radicals..” are still use the word. There is one revision in the revised manuscript. “NH_4^+ and NO are photochemically oxidized on TiO_2” is Modified to “NH_4^+ and NO are photocatalytically oxidized on TiO_2”.

3.Line 232-233, the photodegradation of HCHO on TiO_2 is not zero-order reaction kinetics, the curve is not a line as shown in Figure S6, which decreased slowly and then fast. The reason for it should be the large amount of adsorption of HCHO on the particle during the long-time injection of HCHO. Besides, the continuous wall loss of particle would result in the change of kinetic coefficient. The concentration of particles and HCHO were too high, and the injection time was too long to give clear kinetic parameters. Generally, the photocatalytic process is supposed to be a first order reaction.

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches.

(1)Regarding the question of reaction kinetics

We fitted the photocatalytic degradation curves of HCHO on TiO_2 and KNO_3-TiO_2 using the data of Figure S6 in the original manuscript for zero-order reaction and first-order kinetics, respectively. As shown in Figure 10 below, for both

TiO_2 and KNO_3-TiO_2 systems, the correlation coefficients (R^2) of the zero-order fitting is larger than that of the first-order fitting, so the photocatalytic degradation of HCHO on TiO_2 and KNO_3-TiO_2 fit zero-order kinetics. In order to show the curves more clearly, we marked the KNO_3-TiO_2 line in red color with the new figure shown as Figure S7 in the revised manuscript (Figure 11 below).

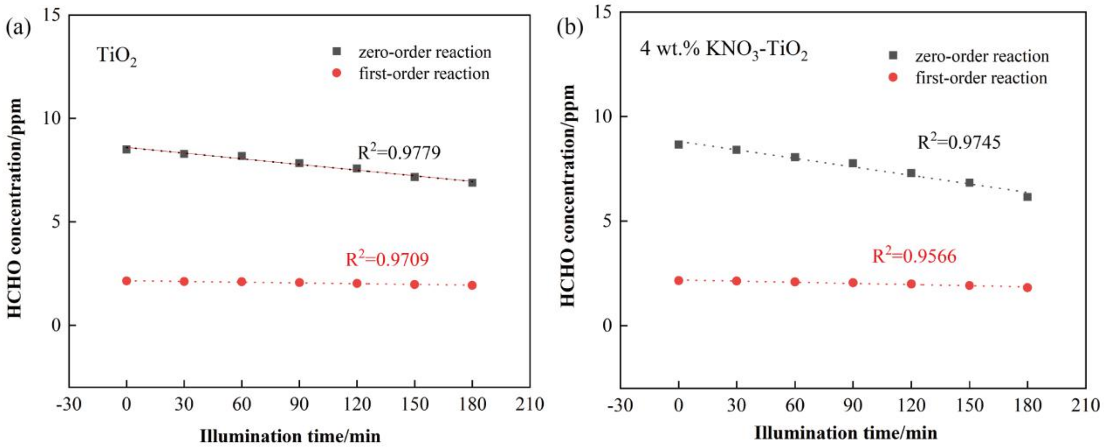

Figure 10. The comparison of correlation coefficients of zero- and first-order reaction curves. The reaction systems are "HCHO + TiO_2" (a) and "HCHO + 4 wt.% KNO_3-TiO_2" (b), both under 365 nm LED lamps at 293 K and 0.8% of relative humidity.

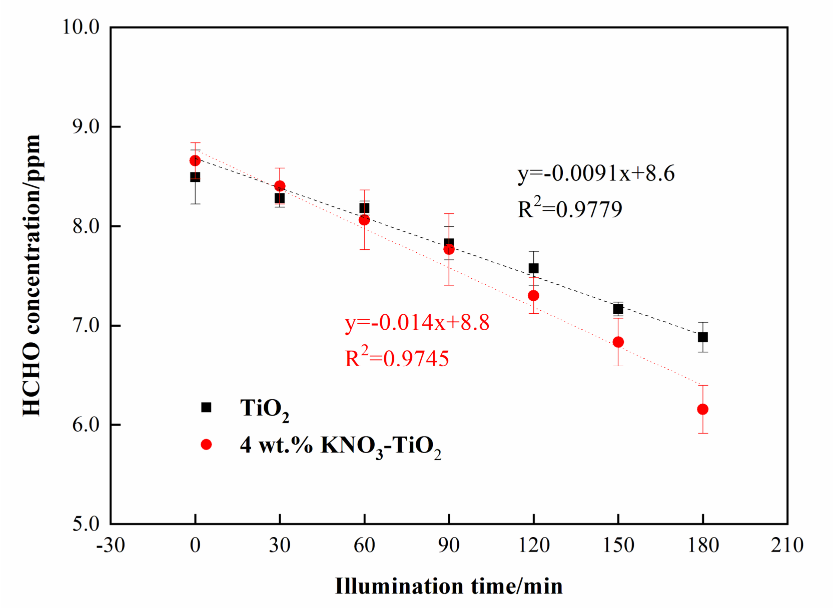

Figure 11. Photocatalytic degradation curve of HCHO on TiO_2 and 4 wt.% KNO_3-TiO_2 particles under 365 nm LED lamps at 293 K and 0.8% of relative humidity.

(2)Regarding the question of possible change of kinetic coefficient

As shown in Figures 3-5 above, the particle size distribution in the chamber can be maintained for several hours, with the number concentration in the chamber decreased by no more than 10% per hour. In addition, the good correlation coefficient of 0.9779 and 0.9745 for TiO_2 and KNO_3-TiO_2, respectively, shown in Figure 11 also reflected that the kinetics fitting and rate constants are believable.

(3)Regarding the injection time and the adsorption of HCHO

We are sorry to make the reviewer misunderstand the operation sequence of the experiment. Figure S3 in the original manuscript is the conditional experiment results to show the HCHO adsorption in the dark before and after particles injection. We think it is Figure S3 that make the reviewer misunderstand. So we modified Figure S3, shown below as Figure 12. The operation sequence of the experiment is as follows. HCHO gases was flowed 10 min into the clean chamber firstly under dark conditions. As can be seen in Figure 12, HCHO can get equilibrium around 90 min. After that, no obvious decrease of HCHO was observed meaning that no further HCHO was adsorbed by the chamber. Then the particles were introduced into the chamber instantly. The concentration of HCHO began to decrease upon particles injection and need 60 min to reach its second adsorption equilibrium. After that, HCHO concentration can be maintained in the dark for several hours, indicating no further adsorption of HCHO by the chamber and the particles. In irradiation experiments, we waited for both HCHO and particles to reach stable before turning on the lights. The related description of the operation has been revised in the manuscript.

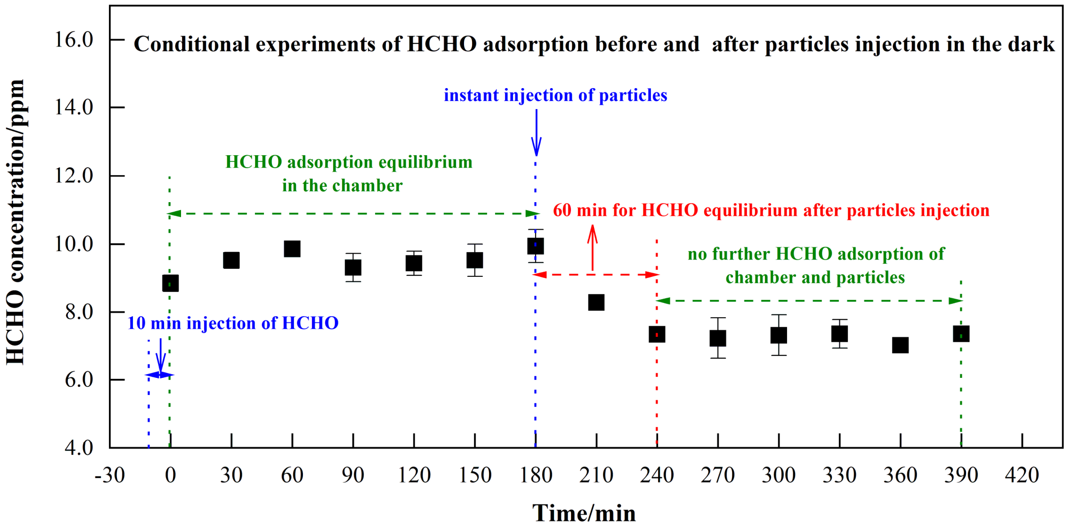

Figure 12. The conditional experiments of HCHO concentration in the environmental chamber in the dark before and after the introduction of particles over time.

4.I can't understand why the authors used KNO_3 and HNO_3 to mixture with TiO_2. In Ma's work, they indicated the NOx concentration formed from KNO_3 was the lowest. KNO_3 only accounts for small proportion in the atmospheric particles. HNO_3 is acid species and can react with TiO_2, which would result in the component changes in this mixture particles. I think that the components in this mixture particles were different from the discussion in the article.

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

(1)I can't understand why the authors used KNO_3 and HNO_3 to mixture with TiO_2. In Ma's work, they indicated the NOx concentration formed from KNO_3 was the lowest. KNO_3 only accounts for small proportion in the atmospheric particles.

Response:

Although KNO_3 accounts for small proportion in the atmospheric particles, it is also important for atmospheric chemistry studies. Wang et al (Sci. Total Environ., 2019, 660: 47-56) found that in winter haze episodes, the formation of KNO_3 particles in the droplet-mode plays an important role in the increase of $PM_{2.5}$ concentration. So the KNO_3-related chemical reactions are important for the study of high pollution weather. In addition, in laboratory studies of nitrate photolysis, KNO_3 is still used as a model particle. For example, Yang et al (EP, 2018, 243: 679-686) used KNO_3 to study the effect of nitrate photolysis on HONO formation in the presence of humic acid; Xu et al (JES, 2021, 102: 198-206) used KNO_3 to study the effect of TiO_2 crystal structure on NO_2 and HONO emission from the nitrates photolysis.

In our study, NH_4NO_3 was also used for the study and the results were compared with those of KNO_3 to investigate the effect of cations on the photocatalytic renoxification process (as discussed in section 3.3.1). Similar to Ma's findings, lower NO_x release was observed from KNO_3 composite compared to NH_4NO_3 composite.

We think this result may be caused by the blocking effect of K^+ on NO_3^-, which has been explained in the original manuscript text line 211-215.

(2)HNO_3 is acid species and can react with TiO_2, which would result in the component changes in this mixture particles. I think that the components in this mixture particles were different from the discussion in the article.

Response:

Some researches characterized the structure of TiO_2 after acid treatment and found no changes. For example, Wang et al. (J Mater Sci: Mater Electron, 2021, 32: 21083) treated TiO_2 with 98% concentrated sulfuric acid for 12 h, and demonstrated by XRD and XPS that acid treatment does not change the structure, elemental composition and chemical state of TiO_2 (Figure 13 below). In our experiment, a low content of HNO_3 (0.002 mol) was used to avoid the possible changes in composition of TiO_2. So it is estimated that the components of the particles would not change. We will make structure characterization to ensure this in our future study.

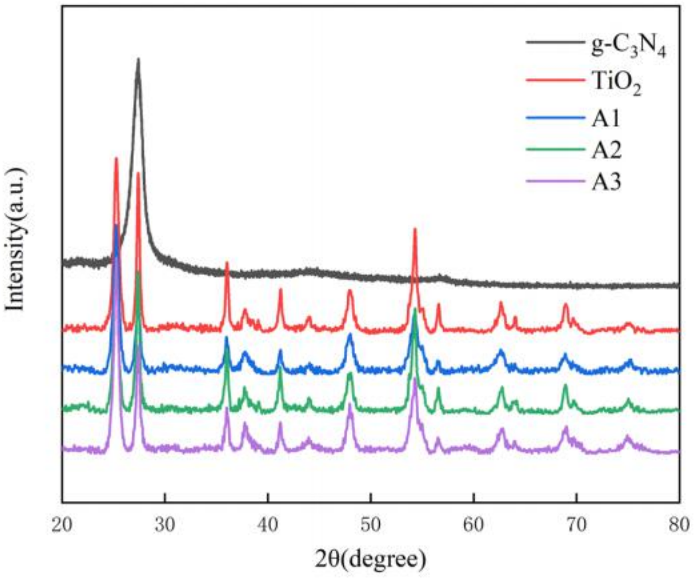

Figure 13. XRD images of TiO_2 nanotubes, g-C_3N_4, A1, A2 and A3. (A1: TiO_2 nanotubes after 12 h of H_2SO_4 treatment; A2: acid-treated TiO_2 compounded with g-C_3N_4; A3: TiO_2 without acid treatment compounded with g-C_3N_4) (J Mater Sci: Mater Electron, 2021, 32: 21083)

5.OH radical was measured by ESR in this study. However, the role of OH radical has not been discussed. And the OH radical generated in different particles and under different conditions have not been compared and analyzed. Besides, NO_3 radical was proposed to be the important intermediates in the reaction. Why did not the authors measure NO_3 radical?

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. The detection of OH radicals is for TiO_2 and Arizona dust, which is intended to demonstrate that photocatalysis process in these two particles do exist. In particular, the presence of OH radicals in the Arizona dust upon irradiation provides evidence that the findings of our study have practical implications. The emergence of NO_x observed in the chamber demonstrated that HCHO promoted the renoxification of ATD particles (Figure S9 in the original manuscript). This result suggests that mineral dust containing photocatalytic semiconductor oxides such as TiO_2, Fe_2O_3, and ZnO could promote the conversion of granular nitrate to NO_x in the presence of HCHO. The above discussions have been given in the original manuscript in lines 298-310.

TiO_2 produces OH radicals under UV illumination, which is well established in the field of photocatalysis (Xu et al., Appl. Catal., B, 2018, 230, 194-202). We provide this data to demonstrate that TiO_2 can be excited under our irradiation conditions and will exert its photocatalytic effect. In this case, other samples with TiO_2 as the main component would also generate OH radicals, although the amount may vary, but is not the main focus of our study. As what has been suggested, NO_3 radicals (coming from h^+ with NO_3^-) is the key species responsible for the formation of large amounts of NO_x. Unfortunately, NO_3 radical was not detected currently due to instrument limitations. Such measurement will be considered in our future studies. However, as discussed in the manuscript, the presence of NO_3 radicals was indirectly illustrated.

6.Weight percentage was used to quantify nitrate in the mixed particle. However, different nitrate has different molecule weight, which would result in that the molar concentrations of different nitrates with the same weight percentage were different. For example, the molar concentration of N in 4 wt % HNO_3-TiO_2 is higher than that of N in 4 wt % KNO_3-TiO_2. This effect should be considered in the formation of NOx.

Response:

Thank you for your comments, which will be all valuable and very helpful for revising and improving the manuscript. We agree with the reviewers that different nitrates with the same weight percentage owns the difference in mole of N, which will cause the difference in NO_2 formation. To exclude this effect, we replotted Figure 2 of the original manuscript (here Figure 14 shown below) with mole normalized ppb as the NO_2 formation unit rather than ppb. As can be seen from Figure 14, the main conclusion is the same, with HNO_3–TiO_2 presented much higher activity than KNO_3–TiO_2 in the presence of HCHO. The discussion related to this Figure has been modified in the revised manuscript.

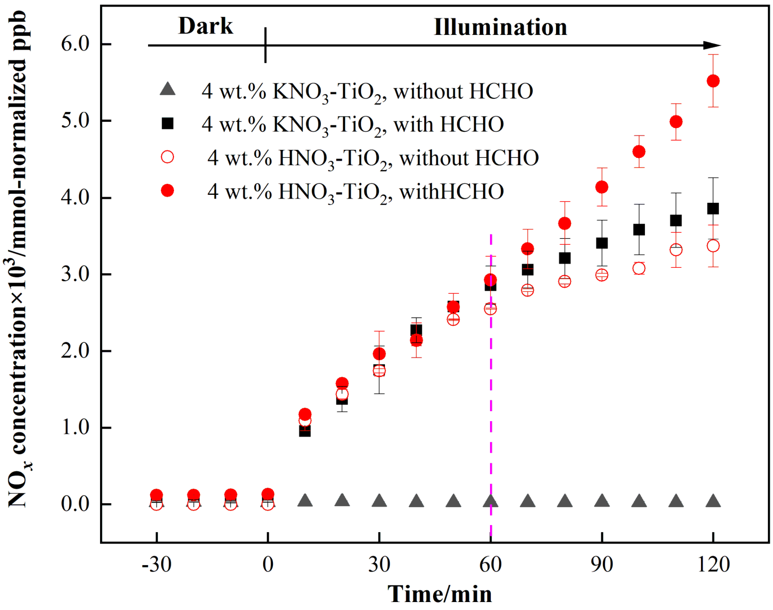

Figure 14. Effect of formaldehyde on the renoxification processes of different nitrate-doped particles at 293 K and 0.8% of relative humidity. 365 nm LED lamps were used during the illumination experiment. The initial concentration of HCHO was about 9 ppm.

Special thanks to you for your good comments.