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Photo-induced Production of Chlorine Molecules from Titanium Dioxide Surfaces Containing Chloride

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Abstract: Titanium dioxide (TiO₂) is extensively used with the process of urbanization, and potentially influence the atmospheric chemistry, yet unclear. In this work, we demonstrated strong production of Cl₂ from illuminated KCl-coated TiO₂ membrane, and suggest an important daytime source of chlorine radicals. We found that water and oxygen were required for the reactions to proceed and Cl₂ production increased linearly with the amount of coated KCl, the humidity of carrier gas and the light intensity. These results suggested that water promotes the reactivity of coated KCl via the interaction with the crystal lattice to release free chloride ions (Cl⁻). The free Cl⁻ transfer charge to O₂ via photoactivated TiO₂ to form Cl₂ and probably O₂⁻ radical. In addition to Cl₂, ClO

and HOCl were also observed via the complex reactions between Cl/Cl₂ and HO_x. An intensive campaign was conducted in Shanghai, during which evident daytime peak of Cl₂ was observed. Estimated Cl₂ production from TiO₂ photocatalysis can be up to 0.2 ppb/h, which were significantly higher than the photolysis of ClNO₂ and highly correlated to the observed Cl₂. Our results suggest a non-negligible role of TiO₂ in atmospheric photochemistry via altering the radical budget.

INTRODUCTION

Titanium dioxide (TiO₂), as the best photocatalyst, has been widely used in environmental remediation¹ and construction materials^{2,3}. The utilization of active TiO₂ for self-cleaning⁴⁻⁶ or purifying atmospheric pollutants⁷ increased significantly with the process of urbanization in recent years. These TiO₂-containing materials, as well as the TiO₂-containing particles such as dust⁸ and combustion particles⁹ can play increasing role in the atmospheric chemistry¹⁰⁻¹³. For example, the TiO₂ induced heterogeneous photochemical processes can promote the formation of several atmospheric oxidants, including HONO^{14,15}, O₃¹¹, possibly NO₃^{8,16}.

Atmospheric Cl radical, known as produced from the photolysis of Cl₂ and nitryl chloride (ClNO₂), is an important atmospheric oxidant¹⁷, and influence the ozone and secondary aerosol formation¹⁸⁻²⁰. Although concentrations of Cl radicals are typically lower than those of other atmospheric radicals, they can react with most atmospheric volatile organic compounds (VOCs) faster than hydroxyl radical (OH)²¹ and therefore play an important role in the atmosphere¹⁹, especially in coastal²² and polluted urban areas^{20, 23, 24}. The source of ClNO₂ is generated via the heterogeneous reaction of nitrogen pentoxide (N₂O₅) with particulate chloride²⁵. However, there is no consensus on the main sources of Cl₂^{17, 26}. Although it is traditionally believed that Cl₂ should decrease after sunrise due to its fast photolysis, several recent observations have reported evident daytime peaks of Cl₂, suggesting a considerable source of light-activated reactions²⁷⁻²⁹ and possible contribution from photochemical sources. Herein, we report the first direct laboratory observation which confirms that TiO₂-mediated

photocatalytic reactions lead to the production of Cl_2 , and a few other chlorinated species.

MATERIALS AND METHODS

Sample preparation. A suspension with 50 ml of KCl solution and 0.1 g of TiO_2 (Sigma-Aldrich, 21 nm primary particle size, $\geq 99.5\%$ trace metals basis, product number: 718467) was prepared to homogeneously coat KCl on TiO_2 particles. The TiO_2 particles in the suspension were then filtrated onto a 50 mm quartz membrane using a water vacuum pump. The membranes were then dried at 323 K before being used in the experiment. Samples with KCl/ TiO_2 mass ratios of 0.0003 g/g, 0.0006 g/g, 0.003 g/g, 0.0057 g/g, 0.015 g/g, 0.028 g/g and 0.06 g/g were prepared. The amount of KCl coated on TiO_2 was measured by ion chromatography. A photo of a prepared sample is shown in Fig. S1.

Laboratory experiments. Fig. S2 shows a schematic of the experimental setup of a flow reactor system. The temperature of the system is kept at 293 K. Ultrapure air and nitrogen were used as the carrier gas, which was separated into a dry air flow and a wet air flow. The RH of the inflow to the reactor was adjusted by changing the ratio of dry air to wet air. Four UV lamps were mounted close to the tube, two of which (1 and 2) are used in all the experiments with irradiance of 16.3 W/m^2 , except for the experiment testing the role of light intensity. The spectrum of the UV lights is shown in Fig. S3. The irradiance increased from 8.4 to 35.1 W/m^2 from one lamp to four lamps, which covered realistic ranges of solar UVA irradiance during the Shanghai campaign (Fig. S4). The temperature and RH inside the flow tube were monitored continuously. Three instruments, namely, a methyl iodide chemical ionization mass spectrometer (I-CIMS), a NO_x analyzer and an O_3 analyzer (Text S1), were used to measure Cl_2 and related species in the outflow from the tube. Four experiments were conducted during the lab campaign, and in each of them we varied a single experimental parameter, including coated KCl amounts, RH of the carrier gas, light irradiance and carrier gas types.

RESULTS AND DISCUSSION

Photo-induced production of Cl₂ from KCl-coated TiO₂. The main conclusion of the abovementioned experiments is that significant production of Cl₂ occurred in the presence of UV irradiation of a KCl-coated TiO₂ membrane. As shown in Fig. 1, we observed a strong production of Cl₂, up to 4-5 ppbv, from an irradiated sample, of which the KCl/TiO₂ ratio was 0.028 g/g and the RH of the carrier gas was 66%. The decrease in Cl₂ concentration indicated fast consumption of the coated KCl. The blank was obtained in many reference experiments, including using a blank membrane, a pure TiO₂ sample and a pure KCl sample, all of which did not show a noticeable increase of Cl₂. This confirms that Cl₂ was produced from the illuminated TiO₂ surfaces containing chloride.

A series of experiments were repeated with varying conditions to investigate the underlying mechanism of Cl₂ production and its dependence on potentially relevant parameters. An experiment testing the role of the amount of KCl coated on TiO₂ was carried out under three different RH values of 9.6%, 38% and 66%, representing very dry to slightly wet environments. The result at 66%, a more atmospherically relevant value, is shown in Fig. 2a. The results at the other RH values are shown in Fig. S5. The observed Cl₂ concentration increased linearly as the KCl/TiO₂ ratio increased from 0.0003 g/g to 0.0057 g/g and reached a plateau thereafter (Fig. 2a). The differences in both the production efficiency and saturated concentrations of Cl₂ among RH values of 9.6%, 38% and 66% were within the experimental errors, indicating that water is not a limiting factor in atmospherically relevant conditions.

Fig. 3 shows a comparison of Cl₂ production among different carrier gases, namely, dry nitrogen gas, wet nitrogen gas (RH = 38%), dry air and wet air (RH = 9.6%). Cl₂ cannot be observed with nitrogen carrier gas under both dry and wet conditions; instead, it is observed only in the system with wet air as the carrier gas. These results suggest that both water and oxygen are required in the reactions. To further investigate the potential role of water in the reaction, a humidity gradient experiment was conducted by changing the RH of the carrier gas from 0% to 88%. Similar to the dependence on the amount of coated KCl, the Cl₂ concentration increased linearly with the RH before

reaching a plateau (Fig. 2b), indicating that water is either a reagent or a factor influencing the activity of the reagent (chloride).

Free Cl^- are believed to be necessary in the reactions to provide electrons to the valence band of photoactivated TiO_2 . KCl can form crystals of $(\text{KCl})_6(\text{H}_2\text{O})_n$ with very little water and release free Cl^- from the edge of the crystal lattice. This separation could be promoted by the number of water molecules, as solvent-shared ion pairs $[\text{K}^+(\text{H}_2\text{O})\text{Cl}^-]$ are formed with 3-9 water molecules, whereas solvent-separated ion pairs (K^+ and Cl^-) can be observed with 10-15 water molecules³⁰. This behavior explains why water can promote the reaction at a value much lower than the deliquescence RH of KCl . Cl_2 production would be determined by both the intensity of illumination and the amount of free Cl^- , which is influenced by both KCl and water. Under certain light irradiance, Cl_2 production will be linearly dependent on the level of free Cl^- (either KCl or water) before reaching a plateau where Cl_2 production is saturated and limited by the irradiance (Fig. 2a and 2b).

To test whether the observed plateau for Cl_2 production is due to the limitation of light irradiance and the relationship between them, we carried out an experiment in which the light number was adjusted from 4 to 1. The results showed that the concentration of Cl_2 produced linearly correlated with the light number and can reach greater than 10 ppbv (Fig. 2c), suggesting that the observed plateau of Cl_2 concentration in both the RH and coated KCl experiments is due to the Cl^- being saturated under a fixed light irradiance (2 UV lights, 16.3 W/m^2).

In addition to Cl_2 , we also observed the production of ClO and HOCl under 66% RH, which showed similar dependence on the amount of coated KCl as did Cl_2 (Fig. 2d). The results of 38% RH are shown in Fig. S5. ClO is another important halogen radical in the atmosphere, while HOCl can be photolyzed to an OH radical and a Cl radical. ClO is typically believed to be formed via the reaction of Cl radical and O_3 in the atmosphere, which however, was not observed during the experiment, indicating an alternative pathway via the reaction of Cl radical and HO_2 radical to form ClO . Since

HO_x has been demonstrated to be produced from the photolysis of water on the surface of TiO₂³¹⁻³³, the reactions of Cl/Cl₂ with HO_x were thus suspected as the most likely pathway of forming ClO. HOCl can be produced from either the reaction of Cl₂ and OH or the reaction of ClO and HO₂. Note that HOCl could react with Cl⁻ ions to reproduce Cl₂. However, the concentration of HClO was too low (more than one order of magnitude) to explain the observed Cl₂ concentration.

In summary, we observed strong production of Cl₂ and moderate production of ClO and HOCl from the photo-induced reaction on KCl-coated TiO₂. A mechanism is proposed as the follows. Water reacts with KCl to release free Cl⁻, which act as the donor to provide the electron to O₂ via the conduction and valence bands of photoactivated TiO₂ and form Cl radical and O₂⁻ radical³⁴. Two Cl radicals combine to form the main product, the Cl₂ molecule. Water is photolyzed to OH and H⁺, which react with O₂⁻ immediately to form HO₂ radicals. The produced Cl₂ further reacts with OH radical to form HOCl. Cl radical reacts with HO₂ to produce ClO radical. Most of the products from this reaction pathway are important atmospheric oxidants (or precursors of oxidants) and thus have the potential to influence atmospheric chemistry.

Atmospheric Implication. In this study, we demonstrated a photo-induced reaction that can produce Cl₂ and in turn influence the atmospheric oxidative capacity by

forming Cl radical and ClO radical. The role of these reactions in the real atmosphere depends primarily on whether there are considerable amounts of chloride-coated TiO₂ materials exposed to the atmosphere. With the process of modern urbanization, TiO₂ containing materials have been widely applied for building exteriors³⁵ (Fig. S7), self-cleaning glasses, road lamps, airport roofs, and road bricks³¹, and easily be exposure to the urban atmosphere. To further identify the role of the above mentioned reactions in the atmosphere, we tested some commercial TiO₂-containing materials, including anatase type TiO₂, rutile type TiO₂, self-cleaning glass, photocatalytic spray and white pigment. Most of these materials except rutile type TiO₂ can produce Cl₂ with different efficiency (Fig. S8).

In an area like East China where had elevated concentration of atmospheric chloride³⁶ (Fig. S9) and increased application of TiO₂ photocatalytic materials²⁹, the chloride chemistry involving TiO₂ may play an important role in the atmospheric chemistry. We conducted a field campaign in the city center of Shanghai, the largest city in China (Fig. 4), to measure the reactive chlorine compounds, including Cl₂ and ClNO₂ using an I-ToF-CIMS, and HCl and Cl⁻ using an online IC system (MARGA). Cl₂ revealed an evident daytime peak, which cannot be explained by the photolysis of ClNO₂ and indicate a missing ubiquitous daytime source of Cl₂. We calculated the production of Cl₂ from TiO₂ involving reactions with the assumption of 0% - 20% of the land surfaces covered by TiO₂-containing materials in urban Shanghai. Estimated Cl₂ production rate from TiO₂ photocatalysis can be up to 0.2 ppb/h (see Text S3), which were significantly higher than the photolysis of ClNO₂ and highly correlated to the observed Cl₂ ($R^2=0.97$). These results confirmed an important role of TiO₂ involved chlorine chemistry in the atmosphere. However, we can't ensure that this uncertainty range, and need some more statistic collection work get more details about urban usage of TiO₂. With the establishment of emerging cities and the use of photocatalytic environmentally friendly materials, this factor may be even higher in the future.

ASSOCIATED CONTENT

Supporting Information

A photo showing the prepared sample of KCl coated TiO₂ (Figure S1). The schematic of the experimental setup of a flow reactor system (Figure S2). Light spectra of the UV lamp (Figure S3). Diurnal variation of UVA during the Shanghai campaign (Figure S4). Dependence of the Cl₂ concentration as a function of the amount of coated KCl with the RH of carrier gas at (a) 9.6%, and (b) 38% (Figure S5a and b); (c) Dependence of the ClO and HOCl as a function of the amount of coated KCl with the RH of carrier gas at 38% (Figure S5c). Location of the measurement site (Figure S6). Use of exterior wall coatings, production of building coatings and completed construction area from 2000 to 2017 in China (Figure S7). Experiments of some commercial materials containing TiO₂ with a carrier gas of pure air of 66% RH and KCl concentration of 0.01 mol/L (Figure S8). Emission map of chlorine (HCl and particulate chloride) in East China (Figure S9).

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221

222 Figure 1 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)
 223 on a KCl/TiO₂ (0.028 g/g) membrane using ultrapure air. The same blank signal was
 224 given by a tube with a KNO₃-coated membrane.

225

226 Figure 2 Dependence of the Cl_2 concentration as a function of (a) the amount of coated
 227 KCl , (b) the RH of the carrier gas, and (c) the light irradiance. (d) dependence of the
 228 ClO and HClO concentration as a function of the amount of coated KCl . The RH of the
 229 carrier gas was 66% in experiment (a) and (d); a sample with $\text{KCl}/\text{TiO}_2 = 0.028$ g/g was
 230 used in experiment (b); and the light irradiance is represented by the number of lights
 231 in experiment (c). Red circle are all data points; red line is the fitting curve; blue triangle
 232 are the first four data points, and blue line is a linear fit of these first 4 data points.

233

234 Figure 3 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)
 235 on a KCl/TiO₂ (0.028 g/g) membrane with a carrier gas of (a) pure nitrogen with an RH
 236 of 0%, (b) pure nitrogen with an RH of 38%, (c) ultrapure air with an RH of 0%, and
 237 (d) ultrapure air with an RH of 9.6%.

238

239 Figure 4. (a) Diurnal variations of Cl_2 production rate from photolysis of ClNO_2 , the
 240 TiO_2 involved processes, as well as ambient Cl_2 diurnal variation. Filled area represents
 241 a range of Cl_2 from TiO_2 photocatalysis with the assumption of 0% - 20% of the land
 242 surfaces covered by TiO_2 -containing materials in urban Shanghai. (b) The correlation
 243 between Cl_2 production rate from Cl_2 observed data and that from TiO_2 involved
 244 processes when the cover factor is 5%, 10%, 15% and 20% respectively.

245

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For Table of Contents Only (Abstract Graphic)

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