

Photoinduced Production of Chlorine Molecules from Titanium Dioxide Surfaces Containing Chloride

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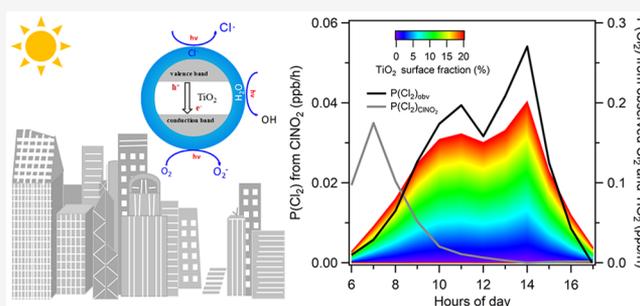


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Supporting Information

ABSTRACT: Titanium dioxide (TiO_2) is extensively used with the process of urbanization and potentially influences atmospheric chemistry, which is yet unclear. In this work, we demonstrated strong production of Cl_2 from illuminated KCl-coated TiO_2 membranes and suggested an important daytime source of chlorine radicals. We found that water and oxygen were required for the reactions to proceed, and Cl_2 production increased linearly with the amount of coated KCl, humidity of the carrier gas, and light intensity. These results suggested that water promotes the reactivity of coated KCl via interaction with the crystal lattice to release free chloride ions (Cl^-). The free Cl^- transfer charges to O_2 via photoactivated TiO_2 to form Cl_2 and probably the O_2^- radical. In addition to Cl_2 , ClO and HOCl were also observed via the complex reactions between Cl/Cl_2 and HO_x . An intensive campaign was conducted in Shanghai, during which evident daytime peaks of Cl_2 were observed. Estimated Cl_2 production from TiO_2 photocatalysis can be up to 0.2 ppb/h when the TiO_2 -containing surface reaches 20% of the urban surface, and highly correlated to the observed Cl_2 . Our results suggest a non-negligible role of TiO_2 in atmospheric photochemistry via altering the radical budget.



INTRODUCTION

Titanium dioxide (TiO_2), as the best photocatalyst, has been widely used in environmental remediation¹ and construction materials.^{2,3} The utilization of active TiO_2 for self-cleaning^{4–6} or purifying atmospheric pollutants⁷ increased significantly with the process of urbanization in recent years. These TiO_2 -containing materials, as well as TiO_2 -containing particles such as dust⁸ and combustion particles⁹ can play an increasing role in atmospheric chemistry.^{10–13} For example, the TiO_2 -induced heterogeneous photochemical processes can promote the formation of several atmospheric oxidants, including HONO,^{14,15} O_3 ,¹¹ and possibly NO_3 .^{8,16}

The atmospheric Cl radical, produced from the photolysis of Cl_2 and nitryl chloride (ClNO_2), is an important atmospheric oxidant¹⁷ and influences ozone and secondary aerosol formation.^{18–20} 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 the hydroxyl radical (OH)²¹ and therefore play an important role in the atmosphere,¹⁹ especially in coastal²² and polluted urban areas.^{20,23,24} The source of ClNO_2 is generated via the heterogeneous reaction of nitrogen pentoxide (N_2O_5) with particulate chloride.²⁵ However, there is no consensus on the main sources of Cl_2 .^{17,26} Although it is

traditionally believed that Cl_2 should decrease after sunrise due to its fast photolysis, several recent observations have reported evident daytime peaks of Cl_2 , suggesting a considerable source of light-activated reactions^{27–29} and possible contributions from photochemical sources. Herein, we report the first direct laboratory observation which confirms that TiO_2 -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

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0.0003, 0.0006, 0.003, 0.0057, 0.015, 0.028, and 0.06 g/g were prepared. The amount of KCl coated on TiO₂ was measured by ion chromatography. A photo of a prepared sample is shown in Figure S1.

Laboratory Experiments. Figure 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) were used in all the experiments with irradiance of 16.3 W/m², except for the experiment testing the role of light intensity. The spectra of the UV lights are shown in Figure S3. The irradiance increased from 8.4 to 35.1 W/m² from one lamp to four lamps, which covered realistic ranges of solar UVA irradiance during the Shanghai campaign (Figure 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 O₃ analyzer (Supporting Information, Section S1), were used to measure Cl₂ 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

Photoinduced Production of Cl₂ from KCl-Coated TiO₂. The main conclusion of the above-mentioned experiments is that significant production of Cl₂ occurred in the presence of UV irradiation of a KCl-coated TiO₂ membrane. As shown in Figure 1, we observed a strong production of Cl₂,

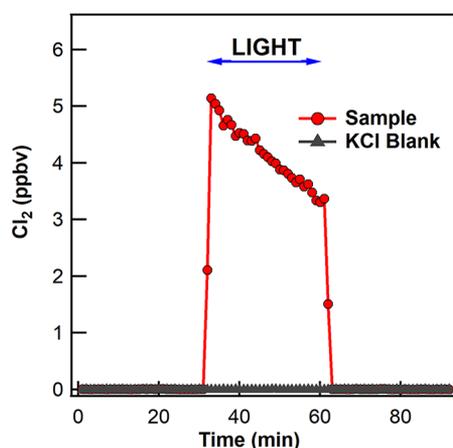


Figure 1. Effect of light (two near-UV-emitting lamps in the 350–400 nm wavelength range) on a KCl/TiO₂ (0.028 g/g) membrane using ultrapure air. The same blank signal was given by a tube with a KCl-coated membrane.

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 in 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 Figure 2a. The results at the other

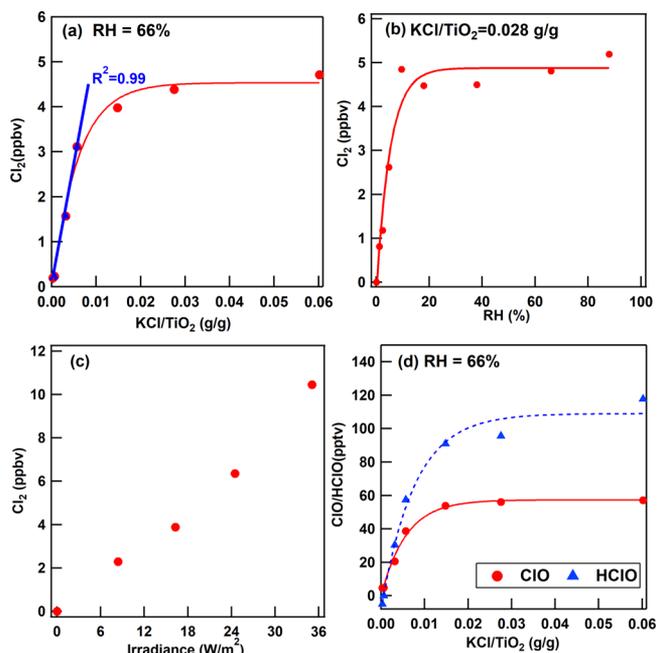


Figure 2. Dependence of Cl₂ concentration as a function of (a) amount of coated KCl, (b) RH of carrier gas, and (c) light irradiance. (d) Dependence of ClO and HClO concentrations as a function of amount of coated KCl. RH of the carrier gas was 66% in experiments (a) and (d). A sample with KCl/TiO₂ = 0.028 g/g was used in experiment (b). In figure (a), red circles are all data points. The red line is the fitting curve. Blue triangles are the first four data points. The blue line is the linear fit of these first four data points.

RH values are shown in Figure S5. The observed Cl₂ concentration increased linearly as the KCl/TiO₂ ratio increased from 0.0003 to 0.0057 g/g and reached a plateau thereafter (Figure 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.

Figure 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 carrier gas from 0% to 88%. Similar to the dependence on the amount of coated KCl, Cl₂ concentration increased linearly with RH before reaching a plateau (Figure 2b), indicating that water is

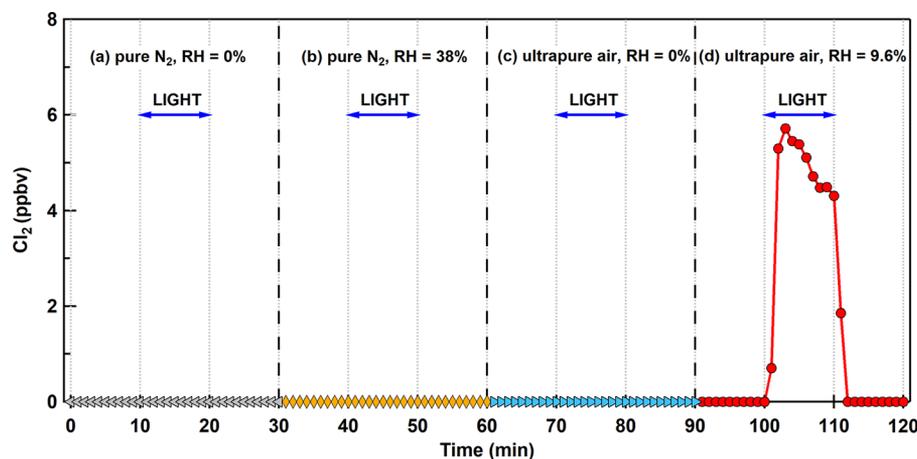


Figure 3. Effect of light (two near-UV-emitting lamps in the 350–400 nm wavelength range) on a KCl/TiO₂ (0.028 g/g) membrane with a carrier gas of (a) pure nitrogen with RH of 0%, (b) pure nitrogen with RH of 38%, (c) ultrapure air with RH of 0%, and (d) ultrapure air with RH of 9.6%.

either a reagent or a factor influencing the activity of the reagent (chloride).

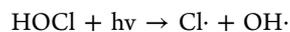
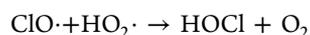
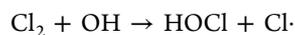
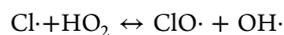
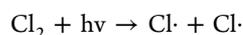
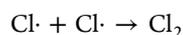
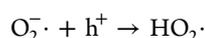
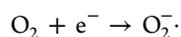
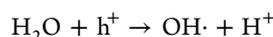
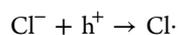
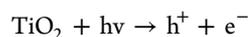
Free Cl⁻ are believed to be necessary in the reactions to provide electrons to the valence band of photoactivated TiO₂. KCl can form crystals of (KCl)₆(H₂O)_{*n*} with very little water and release free Cl⁻ from the edge of the crystal lattice. This separation could be promoted by the number of water molecules, as solvent-shared ion pairs [K⁺(H₂O)Cl⁻] are formed with 3–9 water molecules, whereas solvent-separated ion pairs (K⁺ and Cl⁻) can be observed with 10–15 water molecules.³⁰ This behavior explains why water can promote the reaction at a value much lower than the deliquescence RH of KCl. Cl₂ 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, Cl₂ production will be linearly dependent on the level of free Cl⁻ (either KCl or water) before reaching a plateau where Cl₂ production is saturated and limited by the irradiance (Figure 2a and b).

To test whether the observed plateau for Cl₂ 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 Cl₂ produced linearly correlated with the light number and can reach greater than 10 ppbv (Figure 2c), suggesting that the observed plateau of Cl₂ concentration in both the RH and coated KCl experiments is due to Cl⁻ being saturated under a fixed light irradiance (2 UV lights, 16.3 W/m²).

In addition to Cl₂, we also observed the production of ClO and HOCl under 66% RH, which showed similar dependence on the amount of coated KCl as did Cl₂ (Figure 2d). The results of 38% RH are shown in Figure 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 a Cl radical and O₃ in the atmosphere, which, however, was not observed during the experiment, indicating an alternative pathway via the reaction of the Cl radical and HO₂ radical to form ClO. Since HO_{*x*} has been demonstrated to be produced from the photolysis of water on the surface of TiO₂,^{31–33} 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 1 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 acts as the donor to provide an electron to O₂ via the conduction and valence bands of photoactivated TiO₂ and forms a Cl radical and O₂⁻ radical.³⁴ 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 an OH radical to form HOCl. A Cl radical reacts with HO₂ to produce a 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 photoinduced reaction that can produce Cl₂ and in turn influence the atmospheric oxidative capacity by forming the Cl radical and ClO radical. The role of these reactions in the real atmosphere depends primarily on whether there are consid-

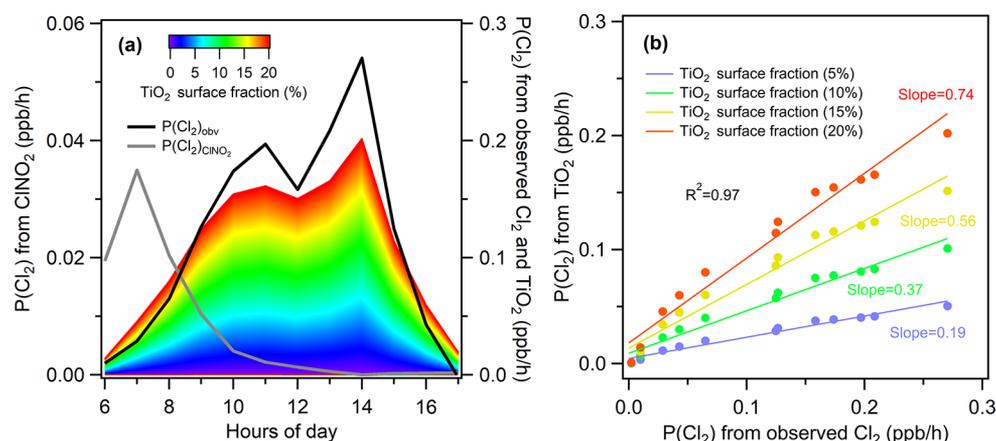


Figure 4. (a) Diurnal variations of observed Cl₂ production rate ($P(\text{Cl}_2)_{\text{obs}}$) during Shanghai campaign; upper limit value of Cl₂ production rate from photolysis of ClNO₂ ($P(\text{Cl}_2)_{\text{ClNO}_2}$) and Cl₂ production rate from TiO₂ photocatalysis ($P(\text{Cl}_2)_{\text{TiO}_2}$) with TiO₂-containing surface fractions from 0% to 20% (color coated). (b) Correlation diagram between observed Cl₂ production rate during Shanghai campaign and Cl₂ production rate from TiO₂ photocatalysis with TiO₂-containing surface fractions of 5%, 10%, 15%, and 20%.

erable 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 (Figure S7), self-cleaning glasses, road lamps, airport roofs, and road bricks³¹ and can be easily exposed 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 efficiencies (Figure S8).

In an area like East China, where there are elevated concentrations of atmospheric chloride³⁶ (Figure S9) and increased application of TiO₂ photocatalytic materials,²⁹ the chloride chemistry involving TiO₂ may play an important role in atmospheric chemistry. We conducted a field campaign in the city center of Shanghai, the largest city in China (Figure 4), to measure the reactive chlorine compounds, including Cl₂ and ClNO₂ using 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 indicated 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 urban surfaces covered by TiO₂-containing materials in Shanghai. The estimated Cl₂ production rate from TiO₂ photocatalysis can be up to 0.2 ppb/h, when the TiO₂-containing surface reached 20% of the urban surface (Supporting Information, Section S3 and S4), and highly correlated to the observed Cl₂. These results confirmed an important role of TiO₂ involving chlorine chemistry in the atmosphere. However, we cannot ensure this uncertainty range and need more statistic collection work to obtain additional 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

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.9b00704>.

Photo showing prepared sample of KCl-coated TiO₂ (Figure S1). Schematic of experimental setup of a flow reactor system (Figure S2). Light spectra of UV lamp (Figure S3). Diurnal variation of UVA during the Shanghai campaign (Figure S4). Dependence of Cl₂ concentration as a function of the amount of coated KCl with RH of carrier gas at 9.6%, and 38% and dependence of ClO and HOCl as a function of the amount of coated KCl with RH of carrier gas at 38% (Figure S5). 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). (PDF)

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Notes

The authors declare no competing financial interest.

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