

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

Yuanyuan Li¹, Wei Nie¹, Yuliang Liu¹, Dandan Huang², Zheng Xu¹, Xiang Peng³, Christian George⁴, Chao Yan⁵, Yee Jun Tham⁵, Chuan Yu³, Men Xia³, Xiao Fu³, Xinfeng Wang⁶, Likun Xue⁶, Zhe Wang³, Zhengning Xu¹, Xuguang Chi¹, Tao Wang³, Aijun Ding^{1,*}

¹ Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, Nanjing, Jiangsu Province, 210023, China

² State Environmental Protection Key Laboratory of Cause and Prevention of Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai, 200233, China

³ Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

⁴ Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France

⁵ Institute for Atmospheric and Earth System Research / Physics, Faculty of Science, University of Helsinki, P. O. Box 64, 00014, Helsinki, Finland

⁶ Environment Research Institute, Shandong University, Jinan, 250100, China

* Correspondence to: Aijun Ding (dingaj@nju.edu.cn)

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

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

34 INTRODUCTION

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

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

56 photocatalytic reactions lead to the production of Cl₂, and a few other chlorinated
57 species.

58 MATERIALS AND METHODS

59 **Sample preparation.** A suspension with 50 ml of KCl solution and 0.1 g of TiO₂
60 (Sigma-Aldrich, 21 nm primary particle size, $\geq 99.5\%$ trace metals basis, product
61 number: 718467) was prepared to homogeneously coat KCl on TiO₂ particles. The TiO₂
62 particles in the suspension were then filtrated onto a 50 mm quartz membrane using a
63 water vacuum pump. The membranes were then dried at 323 K before being used in the
64 experiment. Samples with KCl/TiO₂ mass ratios of 0.0003 g/g, 0.0006 g/g, 0.003 g/g,
65 0.0057 g/g, 0.015 g/g, 0.028 g/g and 0.06 g/g were prepared. The amount of KCl coated
66 on TiO₂ was measured by ion chromatography. A photo of a prepared sample is shown
67 in Fig. S1.

68 **Laboratory experiments.** Fig. S2 shows a schematic of the experimental setup of a
69 flow reactor system. The temperature of the system is kept at 293 K. Ultrapure air and
70 nitrogen were used as the carrier gas, which was separated into a dry air flow and a wet
71 air flow. The RH of the inflow to the reactor was adjusted by changing the ratio of dry
72 air to wet air. Four UV lamps were mounted close to the tube, two of which (1 and 2)
73 are used in all the experiments with irradiance of 16.3 W/m², except for the experiment
74 testing the role of light intensity. The spectrum of the UV lights is shown in Fig. S3.
75 The irradiance increased from 8.4 to 35.1 W/m² from one lamp to four lamps, which
76 covered realistic ranges of solar UVA irradiance during the Shanghai campaign (Fig.
77 S4). The temperature and RH inside the flow tube were monitored continuously. Three
78 instruments, namely, a methyl iodide chemical ionization mass spectrometer (I-CIMS),
79 a NO_x analyzer and an O₃ analyzer (Text S1), were used to measure Cl₂ and related
80 species in the outflow from the tube. Four experiments were conducted during the lab
81 campaign, and in each of them we varied a single experimental parameter, including
82 coated KCl amounts, RH of the carrier gas, light irradiance and carrier gas types.

83 RESULTS AND DISCUSSION

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

94 A series of experiments were repeated with varying conditions to investigate the
95 underlying mechanism of Cl₂ production and its dependence on potentially relevant
96 parameters. An experiment testing the role of the amount of KCl coated on TiO₂ was
97 carried out under three different RH values of 9.6%, 38% and 66%, representing very
98 dry to slightly wet environments. The result at 66%, a more atmospherically relevant
99 value, is shown in Fig. 2a. The results at the other RH values are shown in Fig. S5. The
100 observed Cl₂ concentration increased linearly as the KCl/TiO₂ ratio increased from
101 0.0003 g/g to 0.0057 g/g and reached a plateau thereafter (Fig. 2a). The differences in
102 both the production efficiency and saturated concentrations of Cl₂ among RH values of
103 9.6%, 38% and 66% were within the experimental errors, indicating that water is not a
104 limiting factor in atmospherically relevant conditions.

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

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

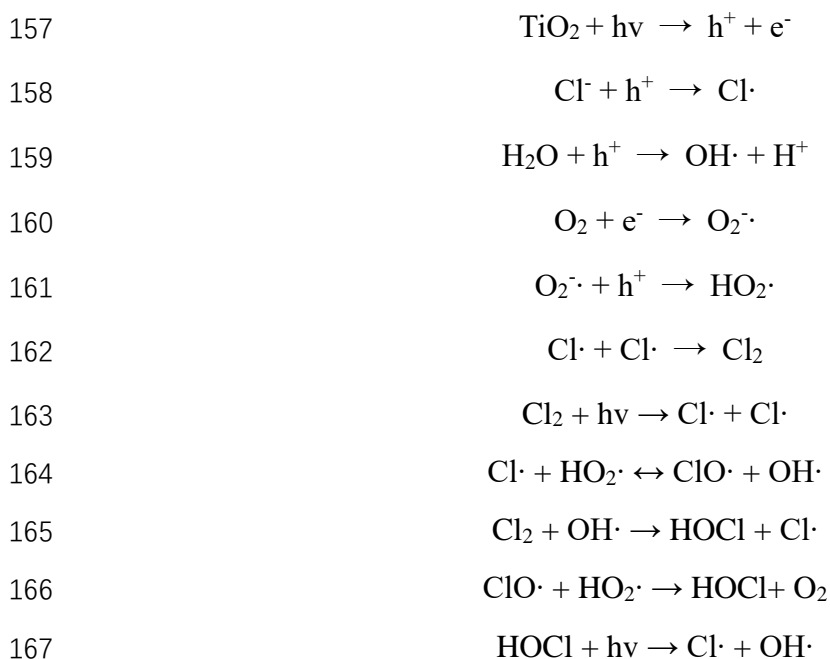
115 Free Cl^- are believed to be necessary in the reactions to provide electrons to the valence
116 band of photoactivated TiO_2 . KCl can form crystals of $(\text{KCl})_6(\text{H}_2\text{O})_n$ with very little
117 water and release free Cl^- from the edge of the crystal lattice. This separation could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

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

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

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

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



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

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

180 In an area like East China where had elevated concentration of atmospheric chloride³⁶
181 (Fig. S9) and increased application of TiO₂ photocatalytic materials²⁹, the chloride
182 chemistry involving TiO₂ may play an important role in the atmospheric chemistry. We
183 conducted a field campaign in the city center of Shanghai, the largest city in China (Fig.
184 4), to measure the reactive chlorine compounds, including Cl₂ and ClNO₂ using an I-
185 ToF-CIMS, and HCl and Cl⁻ using an online IC system (MARGA). Cl₂ revealed an
186 evident daytime peak, which cannot be explained by the photolysis of ClNO₂ and
187 indicate a missing ubiquitous daytime source of Cl₂. We calculated the production of
188 Cl₂ from TiO₂ involving reactions with the assumption of 0% - 20% of the land surfaces
189 covered by TiO₂-containing materials in urban Shanghai. Estimated Cl₂ production rate
190 from TiO₂ photocatalysis can be up to 0.2 ppb/h (see Text S3), which were significantly
191 higher than the photolysis of ClNO₂ and highly correlated to the observed Cl₂ (R²=0.97).
192 These results confirmed an important role of TiO₂ involved chlorine chemistry in the
193 atmosphere. However, we can't ensure that this uncertainty range, and need some more
194 statistic collection work get more details about urban usage of TiO₂. With the
195 establishment of emerging cities and the use of photocatalytic environmentally friendly
196 materials, this factor may be even higher in the future.

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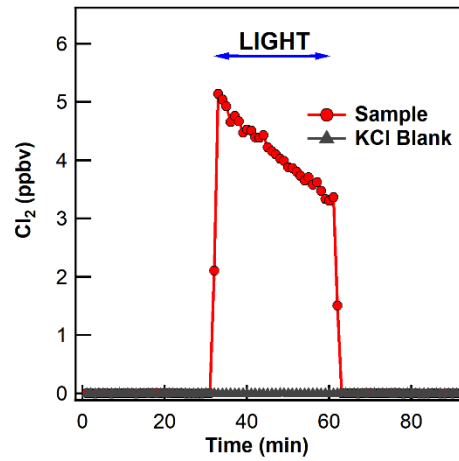
198 **ASSOCIATED CONTENT**

199 **Supporting Information**

200 A photo showing the prepared sample of KCl coated TiO₂ (Figure S1). The schematic
201 of the experimental setup of a flow reactor system (Figure S2). Light spectra of the UV
202 lamp (Figure S3). Diurnal variation of UVA during the Shanghai campaign (Figure S4).
203 Dependence of the Cl₂ concentration as a function of the amount of coated KCl with
204 the RH of carrier gas at (a) 9.6%, and (b) 38% (Figure S5a and b); (c) Dependence of
205 the ClO and HOCl as a function of the amount of coated KCl with the RH of carrier
206 gas at 38% (Figure S5c). Location of the measurement site (Figure S6). Use of exterior
207 wall coatings, production of building coatings and completed construction area from
208 2000 to 2017 in China (Figure S7). Experiments of some commercial materials
209 containing TiO₂ with a carrier gas of pure air of 66% RH and KCl concentration of 0.01
210 mol/L (Figure S8). Emission map of chlorine (HCl and particulate chloride) in East
211 China (Figure S9).

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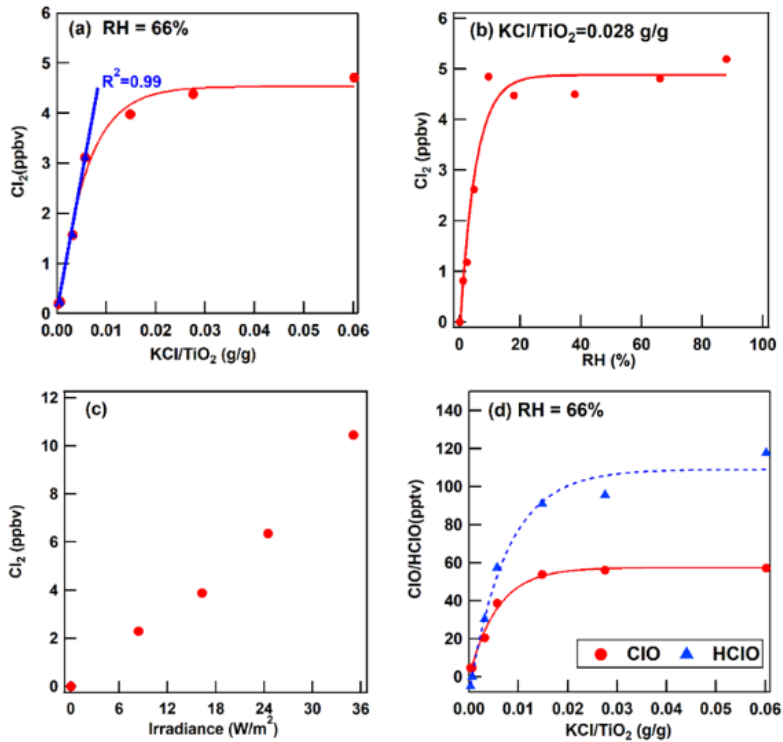


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222 Figure 1 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)

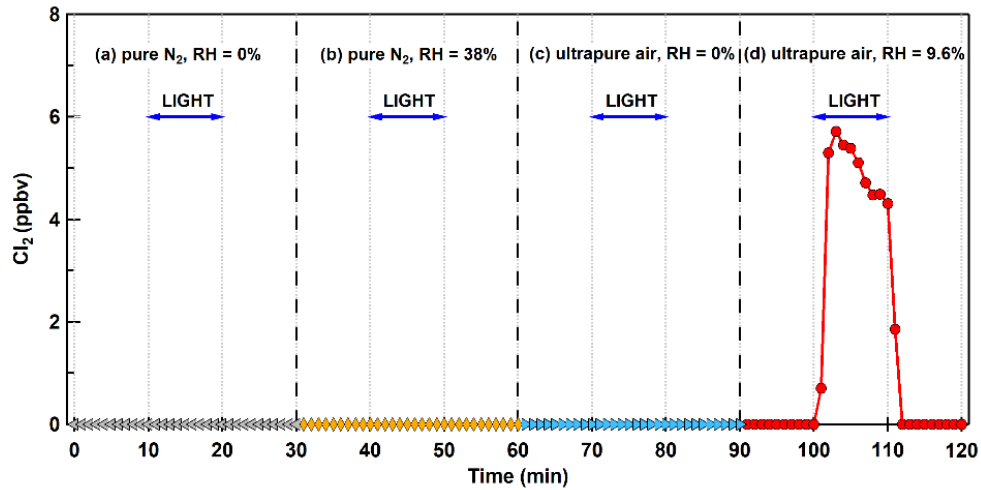
223 on a KCl/TiO₂ (0.028 g/g) membrane using ultrapure air. The same blank signal was

224 given by a tube with a KNO₃-coated membrane.



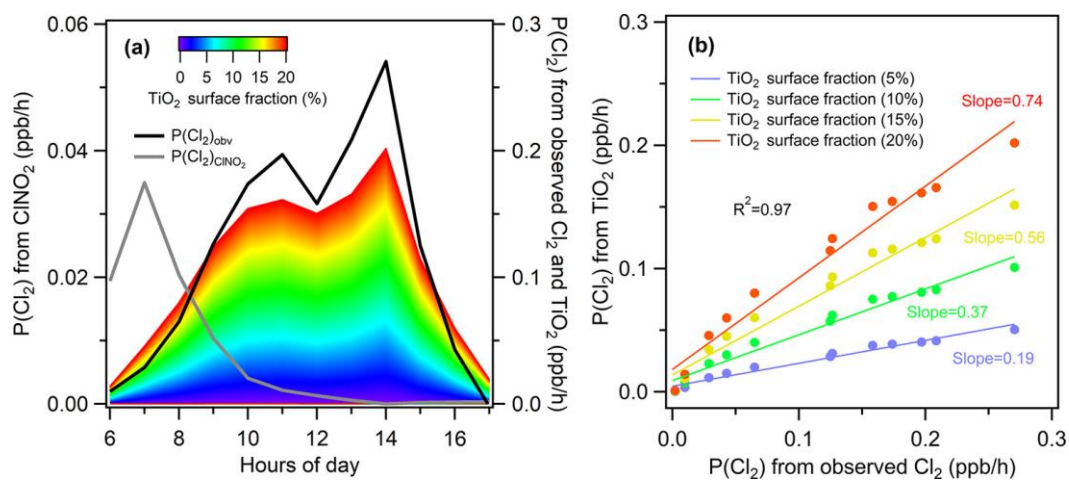
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226 Figure 2 Dependence of the Cl_2 concentration as a function of (a) the amount of coated
 227 KCl , (b) the RH of the carrier gas, and (c) the light irradiance. (d) dependence of the
 228 ClO and HClO concentration as a function of the amount of coated KCl . The RH of the
 229 carrier gas was 66% in experiment (a) and (d); a sample with $\text{KCl}/\text{TiO}_2 = 0.028 \text{ g/g}$ 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.



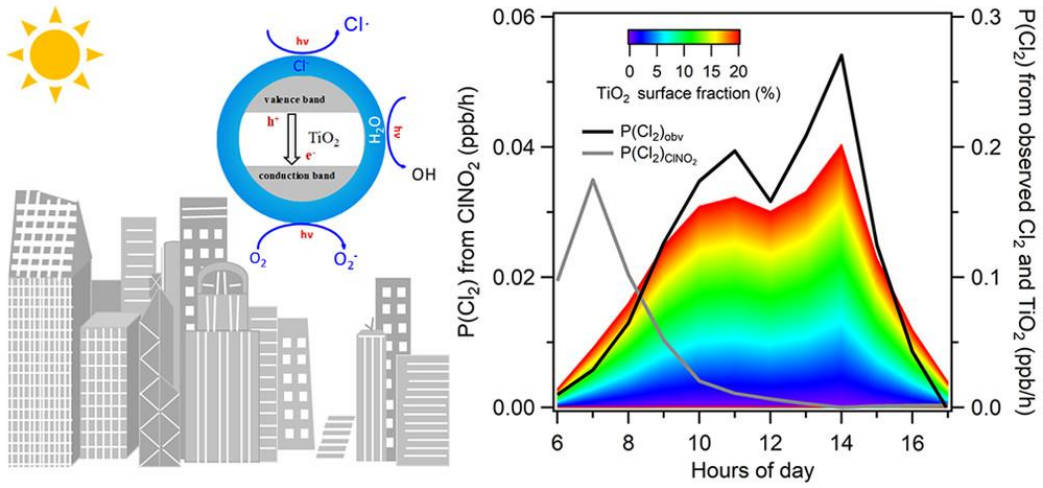
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234 Figure 3 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)
 235 on a KCl/TiO₂ (0.028 g/g) membrane with a carrier gas of (a) pure nitrogen with an RH
 236 of 0%, (b) pure nitrogen with an RH of 38%, (c) ultrapure air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



238

239 Figure 4. (a) Diurnal variations of Cl₂ production rate from photolysis of ClNO₂, the
 240 TiO₂ involved processes, as well as ambient Cl₂ diurnal variation. Filled area represents
 241 a range of Cl₂ from TiO₂ photocatalysis with the assumption of 0% - 20% of the land
 242 surfaces covered by TiO₂-containing materials in urban Shanghai. (b) The correlation
 243 between Cl₂ production rate from Cl₂ observed data and that from TiO₂ involved
 244 processes when the cover factor is 5%, 10%, 15% and 20% respectively.



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For Table of Contents Only (Abstract Graphic)

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