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Photocatalytic removal of NO and NO\textsubscript{2} using titania nanotubes synthesized by hydrothermal method

Nhat Huy Nguyen, Hsunling Bai\textsuperscript{*}

Institute of Environmental Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan, Chinese Taipei.
Email: nhathuy1017@yahoo.com

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A B S T R A C T

In this study, the photocatalysts of titania nanotubes (TNTs) were synthesized at different calcination temperatures using commercial Degussa TiO\textsubscript{2} (P25) as a precursor. The materials were then characterized by BET, SEM, TEM, and XRD analyses. The photocatalytic reactions with NO and NO\textsubscript{2} under UV-A irradiation were both performed. The results showed that the photocatalytic reaction rate of NO was much faster than that of NO\textsubscript{2} and the conversion of NO\textsubscript{2} to nitrate was the rate-limiting step for photocatalytic removal of NO\textsubscript{x} if the nitrate produced cannot be removed continuously from the photocatalyst surface. For TNTs calcined at different temperatures, a significant enhancement was observed on the total NO\textsubscript{x} removal efficiency by TNT calcined at 500\textdegree C for both NO and NO\textsubscript{2} photocatalytic reaction, which could be attributed to its high anatase crystallinity as well as high surface area. These two factors affect primarily on the NO\textsubscript{2} conversion step in which the high anatase crystallinity could be responsible for the high efficiency at the beginning, while the high surface area could be accounted for retaining this high efficiency from nitric acid poisoning during the test period.

Introduction

Indoor air pollution is considered as a significant risk source for human health. The control of indoor air quality is important because people spend most of their life time in the indoor environment (WHO, 2010). Among the emerging technologies for indoor air pollution control, photocatalysis seems to be the best candidate for adsorption and decomposition of indoor air pollutants, which are low concentration but comprise of wide and varied range of pollutant species. Nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}), one of the criteria pollutants regulated by many countries, is a common air pollutant existed in the indoor ambience. Nitrogen dioxide (NO\textsubscript{2}) is associated with a number of adverse effects on human health, particularly in lung and breathing passages.

The removals of NO\textsubscript{x} by photocatalysis using TiO\textsubscript{2}-based materials have been studied extensively (Lasek et al., 2013). In many cases, the photocatalytic oxidation reaction of NO using TiO\textsubscript{2} in the ambient condition was usually suggested and the mechanism was proposed as: NO $\to$ HONO $\to$ NO\textsubscript{2} $\to$ NO\textsubscript{3} (Nakamura et al., 2000; Dalton et al., 2002; Devahasdin et al., 2003). The properties of photocatalyst affecting the NO removal efficiency could include crystal phase, crystal size, surface area, and morphology of the photocatalysts (Hashimoto et al., 2000; Zhang et al., 2010; Ao et al., 2003; Toma et al., 2004). The decrease of total NO\textsubscript{x} removal efficiency during the test period were reported both for NO reaction (Devahasdin et al., 2003; Ohko et al., 2009) and NO\textsubscript{2} reaction (Ohko et al., 2008). Only few authors have considered both NO and NO\textsubscript{2} as the target pollutants in their studies (Ao et al., 2003; Maggos et al., 2007; Laufs et al., 2010; Ballari et al., 2011). Their works have focused either on synthesizing new photocatalytic materials for their effective photocatalysis of NO and NO\textsubscript{2} or on considering...
the effects of environmental factors as well as the reaction products. However, the information about the similarity and the difference between NO and NO\textsubscript{2} photocatalysis are still limited. And the comparison of NO and NO\textsubscript{2} photocatalytic reaction rate as well as the rate-limiting factors have not been reported.

On the other hand, titania nanotubes (TNTs), titanium dioxide with tubular structure, have attracted considerable attention due to their high surface area, high activity and high applicability (Bavykin et al., 2006; Ou and Lo, 2007; Wong et al., 2011). After synthesized by hydrothermal method, the surface area and the value of anatase phase of the TNTs material can be modified by simply calcining TNTs at various temperatures (Yu et al., 2006; Lee et al., 2007; Doong et al., 2012; Jiang et al., 2012). Although TNTs synthesized by hydrothermal method have been studied for many applications and appeared to be promising photocatalysts, no work has been done on the use of them for the photocatalytic removal of NO\textsubscript{x}.

The aim of this research was to study the photocatalytic removals of NO and NO\textsubscript{2} using TNTs as photocatalysts. The NO and NO\textsubscript{2} photocatalytic tests were performed for the TNTs as well as its precursor of Degussa P25. A kinetic study was conducted for TNT calcined at 500°C in order to compare the conversion rate of NO and NO\textsubscript{2} in the experiment.

1 Experimental

1.1 TNTs synthesis and characterization

The TNTs used in this study was synthesized by hydrothermal method (Kasuga et al., 1998). In a typical experiment, 6 g TiO\textsubscript{2} (Degussa P25) was mixed and sonicated with 180 mL of 10 mol/L NaOH solution followed by hydrothermal treatment at 135°C for 24 hr in an autoclave. The produced slurry was then filtered and sonicated in 1 L of HNO\textsubscript{3} solution at pH 1.6 (Tsai et al., 2006). After that, the suspension was filtered and washed with DI water several times until the rinsed pH value reached 6.5–7. The material was subsequently dried overnight at 120°C; the receiving material is the as-synthesized TNT or T-1. Finally, it was calcined at 400°C, 500°C, and 600°C for 2 hr in air, and they were named T-4, T-5, and T-6, respectively.

The TNTs materials were characterized by different techniques for probing their microstructure. The BET (Brunauer-Emmett-Teller) specific surface area, pore size, and pore volume were measured by N\textsubscript{2} adsorption-desorption isotherm at 77 K using a surface area and porosity analyzer (ASAP 2020, Micromeritics, USA). The morphology, particle and tube sizes were obtained from a high-resolution scanning electron microscope (SEM) (S-47001, Hitachi, Japan) and a transmission electron microscope (TEM) (JEM-1210, JEOL, Japan). The crystalline nature of TNTs was analyzed by an X-ray diffractometer (XRD) (X’Pert Pro MRD, PANalytical, the Netherlands) equipped with Cu K\alpha; the scan speed was 4°/min and the 2θ angle was from 10 to 80°. The crystal sizes of TNTs were estimated by the Scherrer equation (Musić et al., 1997):

\[
d_{\text{XRD}} = \frac{k\lambda}{\beta \cos \theta}
\]

where, \( k = 0.89 \) is Scherrer constant, \( \lambda = 0.15406 \) nm is the X-ray wavelength, \( \beta \) is full width at half maximum (FWHM), and \( \theta \) is the Bragg angle.

1.2 Photocatalytic experiment

The photocatalytic reactivity of TNTs was studied by using NO and NO\textsubscript{2} as the target pollutants. The sources of NO and NO\textsubscript{2} were from two certified NO and NO\textsubscript{2} cylinders (Jing De Gases Ltd., Taiwan) in which NO at 498 ppm and NO\textsubscript{2} at 445 ppm were balanced in N\textsubscript{2} and Ar, respectively. The concentrations of NO and NO\textsubscript{2} were measured by a chemiluminescence NO\textsubscript{x} analyzer (S-5012, SIR, Spain), in which the test results were integrated for every 1 min and recorded for every 20 min during each experiment.

The experimental set-up is shown schematically in Fig. 1. The NO or NO\textsubscript{2} gas was diluted with humidified air and dry air, respectively, in a mixer in order to obtain the inlet NO\textsubscript{x} concentration of 9.75 ± 0.25 ppm and relative humidity (RH) of 55% ± 5%. The NO\textsubscript{x} concentrations were relatively higher than indoor NO\textsubscript{x} level to speed up the experiments. The total mixed flow rate of 400 cm\textsuperscript{3}/min was then introduced to a photoreactor for photocatalytic reaction, which corresponded to a gas retention time of 30 sec.

The photoreactor was made of acrylic resin-type material with an inner dimension of \( L \times W \times H = 46 \text{ cm} \times 5 \text{ cm} \times 1.5 \text{ cm} \). Inside this reactor, a glass plate with a size of \( L \times W \times H = 30 \text{ cm} \times 5 \text{ cm} \times 0.2 \text{ cm} \) was employed as a substrate for photocatalyst coating. The amount of photocatalyst for each experiment was 0.11 ± 0.01 g. The UV light source was provided by 5 UV-A light bulbs (UVA-S 10W, Sparkie, Taiwan). And its intensity measured at the surface of photocatalyst was ca. 1.25 mW/cm\textsuperscript{2}. Temperature of the whole system during the experiments was controlled at 25 ± 2°C in a temperature-controlled cabinet. In a typical experiment, the substrate containing photocatalyst was placed inside the reactor and exposed to UV-A irradiation for 30 min before each experiment. All the experiments of photocatalytic reaction of NO and NO\textsubscript{2} using P25 and TNTs were conducted twice and the average values were reported in this work with the maximum deviations within 11% in terms of NO\textsubscript{x} conversion efficiency for NO reaction and 5% for NO\textsubscript{2} reaction.

The efficiency and selectivity of NO reaction were
calculated as following (it is similar for NO₂ reaction):

\[
\eta_{NO} = \left(1 - \frac{NO_{out}}{NO_{in}}\right) \times 100\%
\]

(2)

\[
S_{NO_2} = \frac{NO_{2, out} - NO_{2, in}}{NO_{in} - NO_{out}} \times 100\%
\]

(3)

\[
\eta_{NO_x} = \left(1 - \frac{NO + NO_2}{NO + NO_2}_{in}\right) \times 100\%
\]

(4)

\[
\eta_{NO_x} = \left(1 - \frac{NO + NO_2}{NO + NO_2}_{in}\right) \times 100\%
\]

(5)

2 Results and discussion

2.1 TNTs synthesis and characterization

The BET results for P25 and TNTs are presented in Table 1, while TEM and SEM results are displayed in Figs. 2 and 3, respectively. These results confirmed that the microstructure of TNTs strongly depends on the calcination temperature. The as-synthesized TNT (T-1) showed tubular structure (Fig. 2) with a high specific surface area of 390 m²/g (Table 1), which was about 7 times larger than that of its precursor P25. The tubular structure could be retained for TNTs calcined below 300°C; however, it started to corrupt at the calcination temperature of around 400°C, at which TNTs gradually transformed to rod-like structure. Then at a higher calcination temperature of 500°C, TNTs totally lost their tubular structure and only rod-like structure was observed, while they became particle-like structure as calcined at 600°C. This change in the microstructure of TNTs as calcination temperature increases resulted in the decreases of their surface area and pore volume, which was similar to those reported in the literature (Yu et al., 2006; Lee et al., 2007; Doong et al., 2012; Jiang et al., 2012).

As can be seen from the XRD patterns for P25 and TNTs in Fig. 4, the peak height and peak area gradually increased with the increase of calcination temperature. Rutile peaks only appear in P25 XRD pattern while only anatase peaks were observed for calcined TNTs. The as-synthesized TNT showed two vague peaks of polytitanic acid structure H₂Ti₃O₇ (Du et al., 2001) or amorphous structure. The crystalline phase and crystalline size of P25 and TNTs are summarized in Table 1. Generally, the crystalline size and crystallinity of TNTs continuously increased with the increase of calcination temperature, which are in agreement with those reported in the literature.
Fig. 2 TEM results of T-1, T-4, T-5, and T-6. Scale = 100 nm. T-1, T-4, T-5, and T-6 refer to Table 1.

Fig. 3 SEM results of T-1 and T-5. Scale = 500 nm.

(Yu et al., 2006; Lee et al., 2007; Jiang et al., 2012). It is also noted that the TNT calcined at 600°C (T-6) was similar to P25 in morphology and surface area but they are quite different in their crystalline phase and pore volume.

2.2 Photocatalytic removal of NO using P25 and TNTs

As shown in Fig. 5a, the NO conversion efficiencies were relatively high and stable for all materials except T-1 over the test period. The photocatalysts of P25 and calcined TNTs were proved as good materials for NO conversion with high efficiencies of over 90%. The stability of NO conversion efficiency during the reaction using P25 was agreed with results reported in the literature (Devahasdin et al., 2003; Liu et al., 2007). On the other hand, only 15% conversion efficiency was achieved by the as-synthesized TNT (T-1). Compared to P25, the conversion efficiencies by calcined TNTs were a bit higher but insignificant. It could be concluded that the conversion of NO was quite fast and likely independent of the type and morphology of TiO$_2$.

Figure 5b displays the total NO\textsubscript{x} removal efficiencies. The NO\textsubscript{x} removal efficiency is in the order of T-5 > T-6 > T-4 > P25 > T-1, which could prove that calcined TNTs have better NO\textsubscript{x} removals than that of P25. The as-synthesized TNT (T-1) showed low NO\textsubscript{x} removal efficiency of 4% during the test period, which may be due to its low crystallinity. At the beginning, NO\textsubscript{x} removal efficiency using P25 was 71%, but then declined drastically to only 4% after 4 hr. The best photocatalyst was T-5 with the highest NO\textsubscript{x} removal efficiency of 99% at the beginning and it was decreased to 43% after 4 hr; however, this is a great enhancement compared to the performance of P25 for NO\textsubscript{x} removal.
The NO$_2$ selectivity for the photocatalytic reactions of NO are given in Fig. 5c. For P25 photocatalyst, the selectivity was low at the beginning (26%) but then went up drastically to 95% after 4 hr, a similar trend was also found for T-4. The T-5 and T-6 photocatalysts showed zero selectivity at the beginning, but their selectivity increased up to 84% and 54%, respectively, after 4 hr during the experiment.

The NO$_2$ selectivity for P25 and calcined TNTs were in the order of P25 > T-4 > T-6 > T-5 while the total NO$_x$ removal efficiencies were reverse (T-5 > T-6 > T-4 > P25). This indicates that calcined TNTs were better than P25 for the total NO$_x$ removal because of their low NO$_2$ selectivity. This is because that the photocatalytic oxidation mechanism follows as: NO $\rightarrow$ HNO$_2$ $\rightarrow$ NO$_2$ $\rightarrow$ HNO$_3$. Clearly, during the photocatalytic reaction of NO, when more HNO$_3$ molecules were formed and built-up on the surface of the photocatalyst, it tends to slow down the conversion rate of NO$_2$ $\rightarrow$ HNO$_3$, which then resulted in more NO$_2$ being released into the gas phase. This explains for the continuous increase of NO$_2$ selectivity which results in the continuous decrease of total NO$_x$ removal during the test period, which are in agreement with those reported by Devahasdin et al. (2003) using P25 TiO$_2$ and. Ohko et al. (2009) using TiO$_2$ thin film. The conversion rates of NO for the cases of P25 and calcined TNTs were very fast and similar; however, their total NO$_x$ removals were quite different. This may be resulted from the different reaction rates at either HNO$_2$ $\rightarrow$ NO$_2$ or NO$_2$ $\rightarrow$ HNO$_3$ steps caused by different photocatalysts; therefore, these reactions might be the rate-limiting steps for the photocatalytic removal of NO.

**2.3 Photocatalytic removal of NO$_2$ using P25 and TNTs**

The total NO$_x$ removals are shown in Fig. 6. The results of photocatalytic NO$_2$ reaction showed a similar trend to those of NO reaction in terms of the total NO$_x$ removal efficiency. A stable efficiency of ca. 24% during the test was observed for the as-synthesized TNT (T-1). While for P25 and calcined TNTs, high efficiencies were observed at the beginning then they were decreased. The decrease in NO$_x$ removal efficiencies is consistent with those reported by Ohko et al. (2008) using TiO$_2$ thin film. The results for NO selectivity (data not shown) revealed that only T-1 converted NO$_2$ to NO, with a stable selectivity of 30% during the experiment. For P25 and calcined TNTs, there was no NO formation in the NO$_2$ photocatalytic reaction. This resulted in the same efficiencies for photocatalytic NO$_2$ conversion and NO$_x$ removal using P25, T-4, T-5, and T-6. Among these photocatalysts, T-5 showed the highest NO$_x$ removal efficiency again, which was 100% at the beginning then decreased to 46% after 4 hr.

As can be observed from Fig. 5b and Fig. 6, the trends of NO$_x$ removal efficiencies are similar in photocatalytic removals of NO and NO$_2$ using P25 or calcined TNTs.
All of these photocatalysts could give high efficiencies at the beginning and then they gradually decreased after 4 hr. This may suggest that the reaction of NO$_2$ → HNO$_3$ could be the limiting step for the photocatalytic removal of NO.

In this study, the crystallinity and the surface area of the photocatalysts could be the key factors for NO$_2$ conversion efficiency, which controls the total NO$_x$ removal efficiency. At the beginning, the NO$_x$ removal efficiency is in the order of: T-5 ≈ T-6 > T-4 ≈ P25 ≫ T-1. This finding leads us to believe that the high anatase crystallinity is an important factor because anatase crystallinity of TNTs is in the order of: T-1 > T-5 > T-4 > P25. The high surface area but low crystallinity of T-1 resulted in its NO$_x$ removal efficiency mainly due to the adsorption effect.

The NO$_2$ conversion and NO production of NO$_2$ reaction are plotted in Fig. 7b. Interestingly, only T-1 would lead to the reduction of NO$_2$ to form NO. Two possible reaction pathways can be proposed for the reduction of NO$_2$ to NO occurred on T-1 even in the absence of UV irradiation:

1. The as-synthesized TNT (T-1) provides a large surface area for adsorption and acts as a catalyst for the reaction to be occurred:

\[
2\text{NO}_2(\text{ads}) + \text{H}_2\text{O}(\text{ads}) \rightarrow 2\text{HNO}_3(\text{ads}) + \text{NO}_3(g)
\]  

2. Without calcination, this material possesses polytitanic acid phase in which the surface is covered by an abundance of OH$^-$ group. In this case, NO$_2$ reacts with Ti-OH via disproportion (Kantcheva et al., 1992):

\[
3\text{NO}_2 + 2\text{OH}^- + \text{O}_2 \rightarrow \text{NO}_3^- + \text{NO} + \text{H}_2\text{O}
\]  

In either Reaction (5) or (6), the as-synthesized TNT (T-1) mainly acts as a catalyst instead of photocatalyst for...
the reduction of NO\textsubscript{2} to NO. This is quite different from NO reaction where photocatalytic oxidation of NO to NO\textsubscript{2} occurred.

### 2.5 Comparison for photocatalytic reaction of NO and NO\textsubscript{2}

The conversion efficiencies of the photocatalytic reaction of NO and NO\textsubscript{2} using P25 and TNTs are summarized in Fig. 8, in which these data were averaged over 4 hr. The photocatalytic NO\textsubscript{2} conversion of T-1 is higher than the photocatalytic NO conversion because of the relatively higher adsorption and catalytic reaction potentials of NO\textsubscript{2}. For P25 and calcined TNTs, the NO conversion is always higher than the NO\textsubscript{2} conversion efficiency.

For NO reaction, the NO conversion of P25 and all calcined TNTs were similar while the total NO\textsubscript{x} removal of the photocatalysts was different from each other. In NO\textsubscript{2} reaction, these photocatalysts showed different efficiencies in both NO\textsubscript{x} removal and NO\textsubscript{2} conversion. In this study, the final product of either NO or NO\textsubscript{2} reaction, HNO\textsubscript{3}, was not removed from the surface during the reaction. As a result, one can also observe that the NO\textsubscript{x} removal efficiencies of NO and NO\textsubscript{2} reactions for P25 and calcined TNTs were not in significant difference.

A Langmuir-Hinshelwood model developed by Hunger et al. (2010) was applied to compare the reaction rates of NO and NO\textsubscript{2} using T-5. The kinetic experiments were done with 6 different inlet concentrations of NO and NO\textsubscript{2} in the range of 1–19 ppm. The disappearance rate of NO\textsubscript{x} (can be NO, NO\textsubscript{2}, or NO\textsubscript{x}) is determined by the following equation:

\[
r_{NOx} = \frac{kK_dC_g}{1 + K_dC_g}
\]

where, \( k \) (mg/(m\textsuperscript{3}·sec)) is the reaction rate constant, \( K_d \) (m\textsuperscript{3}/mg) is the adsorption equilibrium constant, and \( C_g \) (mg/m\textsuperscript{3}) is the corresponding NO\textsubscript{x} concentration.

\[r_{NOx}\] is the calculated conversion/removal rates for NO\textsubscript{x} inlet concentration of 10 ppm.

The inlet and outlet concentration of NO, NO\textsubscript{2} and NO\textsubscript{x} at every 20 min during 4 hr experiment were employed to obtain the \( k \) and \( K_d \) values. These two values were then substituted into Eq. (7) to calculate the reaction rate \( r_{NOx} \) for the reactions at NO\textsubscript{x} concentration of 10 ppm. These results (\( k, K_d, r_{NOx} \)) were finally averaged over 4 hr and presented in Table 2. For NO reaction, the conversion rate of NO (48.5 \( \mu \text{mol}/(\text{m}^3 \cdot \text{sec}) \)) was 3 times faster than the NO\textsubscript{x} removal rate (15.8 \( \mu \text{mol}/(\text{m}^3 \cdot \text{sec}) \)). But for NO\textsubscript{2} reaction, the NO\textsubscript{2} conversion and the NO\textsubscript{x} removal rate are almost the same (14.6 and 15 \( \mu \text{mol}/(\text{m}^3 \cdot \text{sec}) \), respectively). Due to the relatively close value of NO\textsubscript{x} removal rate in the reaction of NO and NO\textsubscript{2}, the NO\textsubscript{x} removal efficiency appeared to be independent of the type of NO\textsubscript{x}. Although further investigation is needed, these results would confirm that the oxidation of NO\textsubscript{2} to nitrate was the rate-limiting step in the photocatalytic removal of NO\textsubscript{x} using P25 and calcined TNTs if the HNO\textsubscript{3} product cannot be continuously removed from the photocatalytic material.

### 3 Conclusions

The photocatalytic reactions of NO and NO\textsubscript{2} were performed and compared for P25 and TNTs photocatalysts. The results revealed that T-5 had a superior photocatalytic activity for both NO and NO\textsubscript{2} reaction in terms of NO\textsubscript{x} removal. Its high efficiency was due to its low NO\textsubscript{2} selectivity, which means that the NO\textsubscript{2} formed from NO can be fast oxidized to HNO\textsubscript{3}. And this is attributed to the relatively high surface area and anatase crystallinity. In addition, the as-synthesized TNT played different major roles in NO\textsubscript{x} removal: as a photocatalyst for the oxidation reaction of NO to NO\textsubscript{2} and as a catalyst for the reduction reaction of NO\textsubscript{2} to NO. The results also showed that the total NO\textsubscript{x} removal efficiency of the photocatalytic oxidation appeared to be independent of the type of NO\textsubscript{x} (NO or NO\textsubscript{2}). The NO conversion rate was much faster than the NO\textsubscript{2} conversion rate, thus the oxidation of NO\textsubscript{2} to nitrate could be the rate-limiting step for photocatalytic
removal of NOx using P25 and calcined TNTs.

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Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Zhiwu Wang
The Ohio State University, China
Yuesi Wang
Institute of Atmospheric Physics, Chinese Academy of Sciences, China

Environmental toxicology and health
Jingwen Chen
Dalian University of Technology, China
Junying Hu
Peking University, China
Guibin Jiang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Sijin Liu
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Tsuyoshi Nakanishi
Gifu Pharmaceutical University, Japan
Willie Peijnenburg
University of Leiden, The Netherlands

Environmental catalysis and materials
Hong He
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Junhua Li
Tsinghua University, China
Wenfeng Shangguan
Shanghai Jiao Tong University, China

Environmental analysis and method
Zongwei Cai
Hong Kong Baptist University, Hong Kong, China
Jiping Chen
Dalian University of Technology, China

Municipal solid waste and green chemistry
Pinjing He
Tongji University, China

Environmental biology
Yong Cai
Florida International University, USA
Henner Holbert
RWTH Aachen University, Germany

Yongmin Han
University of Science & Technology of China

Environmental ecolog
Rusong Wang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Atmospheric environment
Xuejun Wang
Peking University, China
Lizhong Zhu
Zhejiang University, China

Environmental toxicology and health
Jingwen Chen
Dalian University of Technology, China
Junying Hu
Peking University, China
Guibin Jiang
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Regional environment
Christopher Anderson
Massey University, New Zealand
Zaocong Cai
Nanjing Normal University, China
Xinxin Feng
Institute of Geochemistry, Chinese Academy of Sciences, China
Hongjing Hu
Huazhong Agricultural University, China
Kim-Chie Lam
The Chinese University of Hong Kong, Hong Kong, China

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The Chinese University of Hong Kong, Hong Kong, China

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Nanjing Normal University, China
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The Chinese University of Hong Kong, Hong Kong, China

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Shanghai Jiao Tong University, China

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Atmospheric environment
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Peking University, China
Lizhong Zhu
Zhejiang University, China

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