Investigation of the Effect of Aerosolized TiO₂ Nanoparticles on the NO₂ Concentrations under UVA Exposure

Ali Mohamadi Nasrabadi, Ana Maria Todea, Carmen Wolf, Tolga Demirel,
David Habryka, Christof Asbach*

Air Quality & Filtration Unit, Institute of Energy and Environmental Technology e. V. (IUTA),
Duisburg, Germany

ABSTRACT

Engineered nanomaterials (ENM) are utilized and produced during many engineering processes. However, they may generate airborne nanoparticles during different phases of their life cycles. TiO₂, which is known for its photocatalytic properties, especially in terms of degrading NO₂, is one of the most widely produced ENM. Ambient NO₂ stems mainly from vehicular and industrial combustion processes and potentially harms human health upon inhalation. This study investigated the photocatalytic reduction of NO₂ due to varying concentrations of aerosolized TiO₂ nanoparticles during varying levels of ultraviolet A (UVA) exposure. Additionally, we evaluated the effects of low (5%), moderate (35%), and high (70%) relative humidity. Our results demonstrated that the decrease in NO₂ depended on both the TiO₂ concentration and the UVA intensity. However, when the former was high ($> 3.23\text{E}+06\text{ cm}^{-3}$), the contribution of the latter was negligible. On the other hand, when the latter was high, the influence of the former was minimal. Furthermore, as the UVA exposure increased in duration, its effect became dominant over that of the TiO₂ concentration. Finally, we found the relative humidity to be an insignificant factor during conditions with strong UVA (6328 W s m^{-2}).

Keywords: TiO₂ aerosolized nanoparticles, NO₂ reduction, UVA exposure, Uptake coefficient

OPEN ACCESS

Received: October 29, 2020

Revised: January 26, 2021

Accepted: February 6, 2021

* **Corresponding Author:**

asbach@iuta.de

Publisher:

Taiwan Association for Aerosol
Research

ISSN: 1680-8584 print

ISSN: 2071-1409 online

Copyright: The Author(s).

This is an open access article distributed under the terms of the [Creative Commons Attribution License \(CC BY 4.0\)](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are cited.

1 INTRODUCTION

Engineered nanomaterials (ENM) can be released to the environment, including the atmosphere, during many instances throughout the product life cycle (Gottschalk *et al.*, 2011). They can be released into the air, e.g., with the flue gas from an industrial facility where they are produced or processed, during mechanical treatment of a composite with embedded ENM (e.g., sanding of a coating) or during waste incineration. Once airborne, due to their small size and low inertia, ENM can easily disperse over long distances from their emission sources. Only little is known about the release of ENM to the atmospheric environment (John *et al.*, 2017). It was estimated that the amount of ENM used in different industrial applications would rise up to 1,663,000 tons by 2020. Keller *et al.* (2013) reported that 0.1–1.5% of produced ENM are estimated to be released into the atmosphere during their life cycle. While airborne, ENM may interact with gaseous components of the air and affect atmospheric chemistry. Due to the generally high surface-area-to-mass ratio of ENM, even rather low mass concentrations of ENM may have a stronger effect on atmospheric chemistry than their larger counterparts.

Titanium dioxide (TiO₂) is one of the most produced and used ENM worldwide (Piccinno *et al.*, 2012). TiO₂ is chemically inert in the dark, inexpensive, and non-toxic. Nano-sized TiO₂ is widely used for its photocatalytic activity, whereas micron-sized TiO₂ is a common white pigment. Nano-sized TiO₂ is mostly implemented in a solid (e.g., polymer) or liquid (e.g., sunscreen) matrix material, from where strong release into the atmosphere is rather unlikely. It was estimated in

2012 that the global annual production of TiO₂ nanoparticles would be between 500 and 5500 tons, out of which between 55 and 3000 tons would be produced in the European Union (EU; Piccino *et al.*, 2012). Mueller and Nowack (2008) models showed that the amount of TiO₂ nanoparticles in the atmosphere above Switzerland is around 1.5 ng m⁻³. The strongest release of TiO₂ into the atmosphere can therefore be expected from the manufacturing plants, where the materials are produced. When TiO₂ is exposed to UVA light with wavelengths between 320 and 390 nm, photochemical reactions can be initiated at the TiO₂ surface. These reactions have the potential to change the chemical balance of the atmosphere (John *et al.*, 2017). TiO₂ has three major phases, i.e., anatase, rutile, and brookite. Anatase TiO₂ generally provides the highest photocatalytic activity (Augustynski, 1993). However, adding a fraction of rutile TiO₂ in an anatase sample further increases the catalytic activity (Chen *et al.*, 2012). The material used here, i.e., P25 TiO₂ (Evonik AG, Germany), is composed of anatase and rutile phases. Their ratio has been reported to be between 70:30 and 80:20 (Tobaldi *et al.*, 2014).

Nitrogen dioxide (NO₂) is a very common air pollutant, especially in urban areas. NO₂ has been identified to pose a health risk to humans when inhaled, in particular on the respiratory and the cardiovascular system (Kampa and Castanas, 2008). A main source of NO₂ is the transportation sector (diesel engines); around 4% of the urban population of the 28 EU member states (EU-28) was exposed to NO₂ concentrations above the EU annual limit value. According to estimations, the population exposure to NO₂ in the EU-28 in 2018 resulted in around 54,000 premature deaths (Air quality in Europe, 2020). Several regulations are in place to control the exposure of the general public and workers to NO_x. In the EU, the annual limit value for the ambient NO₂ concentration is 40 µg m⁻³.

It is well known that TiO₂ is photocatalytically active in presence of UV light and is capable of reducing nitrogen dioxide (Febo *et al.*, 1995). Recently, titanium dioxide has been widely used in building material, as self-cleaning surfaces, in concrete or glass (Ohko *et al.*, 2008; Langridge *et al.*, 2009; Monge *et al.*, 2010), or as photoactive paints (Devahasdin *et al.*, 2003; Maggos *et al.*, 2007; Laufs *et al.*, 2010) to reduce nitrogen dioxide from the atmosphere. Sodium lamps emitting UV light can be coated with TiO₂ to reduce and decompose NO₂ emissions from vehicles passing through tunnels (Fujishima *et al.*, 2008). Building exteriors coated with TiO₂ are widely used around the world. Ballari *et al.* (2011) experimentally studied NO_x conversion over a photocatalytic concrete stone containing TiO₂. Their results show that NO₂ conversion can increase up to 75%, depending on the UVA irradiance and relative humidity. Laufs *et al.* (2010) studied the decomposition of nitrogen oxides on the surface painted with the commercial photocatalytic paints in a flow tube reactor. Their results show that covered surfaces are an effective sink for NO₂. The reported uptake coefficient in their work under a UVA irradiance of 57 W m⁻² was in the range of 0.5 to 3E-05. Langridge *et al.* (2009) experimentally studied the photocatalytic conversion of NO₂ on commercial self-cleaning window glass panes at different relative humidity values. Their experimental results show that the NO₂ reduction increases from 50% to 70% by increasing the relative humidity from 8% to 45%. Monge *et al.* (2010) reported that the uptake coefficient of NO₂ increased from 2.2E-09 to 1.1E-07 by changing the ratio of TiO₂/SiO₂ mixture film used over coated surfaces from 10% to 100%, which demonstrated the important role of titanium dioxide on the reduction of NO₂. Zein and Bedjanian (2012) investigated the effects of different parameters such as NO₂ concentration, UV irradiance intensity, and relative humidity on the uptake coefficient of NO₂. Zein and Bedjanian (2012) used a tube reactor in which the outer tube surface was coated with TiO₂ to investigate the effects of different parameters such as NO₂ concentration, UV irradiance intensity, and relative humidity on the uptake coefficient of NO₂. Their results showed that the initial reaction rate for relative humidity of 40% is higher than at a relative humidity of 0%. However, by increasing the reaction time, the effect of relative humidity became negligible. The effect of airborne submicron TiO₂ on NO₂ concentration for different ranges of relative humidity was investigated by Gustafsson *et al.* (2006). They reported uptake coefficients in the range of 1.2E-04 and 9.6E-04 for relative humidity between 15% and 80%, intensity of 16 W m⁻², reactive surface of 0.43 m² m⁻³, and NO₂ mixing ratio of 100 ppbv. All showed a clear effect of TiO₂ on NO₂ concentration. However, in the case of aerosolized nanoscale TiO₂, still more investigations are needed. Especially, the effect of reactive surfaces of TiO₂, UVA exposure and exposure time still need to be considered.

The aim of this work was therefore to experimentally study the effect of airborne TiO₂ nanomaterial on NO₂ concentrations. To do so, different concentrations of TiO₂ were examined

under different UV light intensities. Besides, the effect of relative humidity on the NO_2 reduction was investigated by considering different TiO_2 concentrations and UV light exposure.

2 METHODS

2.1 Description of Experimental Set-up

Fig. 1 shows a schematic of the experimental set-up. The experimental set-up consists of a quartz glass tube reactor with an inner diameter of 10.17 cm and length of 200 cm, coaxially installed inside a PVC tube with a diameter of 30 cm and length of 200 cm. Three sequential groups of UV lamps ($\lambda_{\text{max}} = 365 \text{ nm}$; TL-D 18W/08; Philips) are fixed on the inner side of PVC tube. Each group consists of six parallel lamps (in total 18 lamps). The lamps can be individually switched on and off to mimic different exposure times and light intensities. The eventual exposure of the aerosol to UV light is determined by the product of the exposure time and the UVA light intensity. In total, for a given flow rate 18 different but equally spaced exposures can be adjusted with this set-up, determined by the number of active UV lamps.

For producing NO_2 , 0.5 L min^{-1} filtered air was passed through a U-tube in which a permeation tube (VICI Metronics, Inc.) was placed. The temperature of the U-tube with the permeation tube was maintained constant at 30°C by placing it inside a water bath. The 0.5 L min^{-1} NO_2 flow was mixed with 9.5 L min^{-1} filtered air before being introduced into the quartz glass tube. The air flow rates were controlled by two mass flow controllers (GFC17; Aalborg, Orangeburg, NY, USA). To supply air with different relative humidity, a cabin air filter test rig according to ISO/TS 11155 was utilized to provide relative humidity levels of 5%, 35%, and 70%. The concentrations of NO/NO_2 at the inlet and outlet of the reactor were measured using two NO_x analyzers (AC32M; Environnement S.A.). Based on a European air quality standard (Volz-Thomas *et al.*, 2003), the 1-hour NO_2 values must not exceed 120 ppbv. Therefore, a concentration near this value was chosen for the experiments. The TiO_2 ENM were aerosolized from aqueous suspensions of P25 (Evonik Industries AG, Germany) using an atomizer (ATM 226; Topas GmbH), followed by a homemade coaxial, silica-gel-based diffusion dryer. Particle size distributions were measured with a Scanning Mobility Particle Sizer (SMPS; Model 3996; TSI Inc.). The SMPS consists of an 85 Kr aerosol neutralizer (Model 3077A; TSI Inc.), differential mobility analyzer (DMA; Model 3081; TSI Inc.), a water-based condensation particle counter (CPC; Model 3787; TSI Inc.), and an electrical classifier (Model 3080; TSI Inc.).

Fig. 1. Schematic of the experimental set-up.

Under UV light illumination, TiO_2 aerosols can reduce NO_2 to HONO. As HONO is detected by the NO_x analyzers as NO_2 , a Na_2CO_3 denuder was used between the exit of the quartz glass tube and the detector to remove any HONO that might be generated during the experiments to reduce false-positive results. The denuder consists of a quartz glass tube with a length of 55 cm and a diameter of 0.7 cm, that was coated with a solution of: 1% Na_2CO_3 (w/v) + 1% glycerol (w/v) in water-methanol 1:1 solution. The solution was poured into the glass tube, rotated and moved in upward-downward direction for several times at different angles (Febo *et al.*, 1993, 1995; Monge *et al.*, 2010). The total NO_2 trapped in the denuder in the absence of UV exposure was around 3%, which was similar than the value reported by Monge *et al.* (2010).

To estimate the total UV exposure of the aerosol inside the reactor, it is necessary to know both the residence time of the aerosol inside the reactor as well as the UV intensity. The latter was measured using a radiometer (RM-21; Opsytec Dr. Gröbel GmbH, Germany). The sensor measures the UVA intensity in a spectral range from 315 to 400 nm. The measurement was conducted along the center line of the reactor glass tube with only one UV lamp active.

2.2 UVA Exposure inside the Reactor

The experimental results show that the average UVA exposure over the length of one lamp is 12 W m^{-2} . The measurements were repeated by adding the number of active lamps per group and it could be shown that the exposure is additive. For the given flow rate, the actual exposure of the aerosol, i.e., the product of exposure time and UVA intensity, is therefore only determined by the number of active lamps.

Several experiments were carried out to investigate the effect of UVA intensity, exposure length and exposure time. For instance, our experiments showed that for an exposure length of 120 cm (two groups) and two sequential active UVA lamps (one per group), the reduction of NO_2 is identical as with an exposure length of 60 cm (one group) and two parallel active UV lamps. These experiments were repeated for one active lamp in different groups, as well as two, three, and six active lamps in different combinations. Therefore, our results show that the conditions inside the reactor are homogeneous and that the NO_2 reduction as a function of UVA exposure can be easily determined by the number of active lamps.

With the measured data, the UVA exposure (expressed in W s m^{-2}) is calculated as follows:

$$E_{UVA} = N_L I_0 t_0 \quad (1)$$

where E_{UVA} represents the UVA exposure that is the UVA radiant energy emitted over a surface per unit of time, N_L the number of active lamps, I_0 the intensity of one lamp (here 12 W m^{-2}) and t_0 is the exposure time for a single active lamp. The exposure time is calculated as follows:

$$t_0 = \frac{L_l}{v_0} \quad (2)$$

where L_l represents the length of one group of lamps and v_0 the mean airflow velocity:

$$v_0 = \frac{Q}{A} \quad (3)$$

where Q represents the air flow rate and A the cross-sectional area of the quartz glass tube.

With a flow rate of 10 L min^{-1} , a length per group of lamps of 60 cm and a reactor tube diameter of 10 cm, the residence time per group of lamps is 29.2 s and the UVA exposure per active lamp 351.6 W s m^{-2} . The UVA exposure in this study is between 351.6 and 6328 W s m^{-2} . The number of lamps and related intensity and UVA exposure are presented in Table 1.

Table 1. UVA exposure for different numbers of active lamps.

Number of UVA lamps	1	2	3	6	12	18
UVA exposure (W s m^{-2})	351.6	703	1055	2109	4219	6328

2.3 Experimental Set-up Evaluation

The NO₂ reduction in absence of TiO₂ in terms of NO₂ photolysis frequencies (j) was considered to evaluate the experimental set-up. Photolysis frequency was expressed as the rate of NO₂ concentration loss due to the UVA exposure. The photolysis frequency is defined as:

$$j(\text{NO}_2) = -\frac{1}{[\text{NO}_2]} \frac{d[\text{NO}_2]}{dt} \quad (4)$$

where [NO₂] and t represent the NO₂ concentration and exposure time, respectively. The photolysis frequencies (j) of our experimental results are presented in Fig. 2. Similar to Zein and Bedjanian (2012) results, the trend of NO₂ loss was rising along with increasing the number of UVA lamps in absence of TiO₂. In our experiments, $j(\text{NO}_2)$ ranged from 0.0015 to 0.011 s⁻¹ (one to six lamps) which showed a good agreement with Zein and Bedjanian (2012) who reported $j(\text{NO}_2)$ from 0.002 to 0.012 s⁻¹. Bohn *et al.* (2005) reported $j(\text{NO}_2)$ values between 0.0001 and 0.01 s⁻¹ using a simulation chamber as a chemical actinometer under the influence of natural sunlight and Laufs *et al.* (2010) reported this quantity to be below 0.008 s⁻¹ in central Europe. The range of photolysis frequencies in our work is comparable with the corresponding values in the atmosphere as well as previous studies which investigated the reaction between NO₂ and UVA exposure over a coated surface with TiO₂ films. The time series of NO and NO₂ concentration variations under UVA exposure is presented in Fig. S1 (in the supplementary materials).

2.4 Particle Size Distribution

The effect of TiO₂ on the NO₂ concentration was investigated for different UVA exposures at a relative humidity of 5%. The number size distributions of aerosolized TiO₂ particles were measured with the SMPS. The modal diameters of the distributions were 140 nm. The size distribution shown in Fig. 3 represents the average distribution for particle concentrations of 0.47, 1.03, 1.72, and 3.23E+06 cm⁻³, normalized with respect to the total concentration. For each concentration, size distributions were at least measured in triplicate. (The error bars in this study represents the standard deviation of the results obtained in each experiment). By using the SMPS measurements, the reactive surface area concentration (m² m⁻³) (Uekawa *et al.*, 2003) was calculated. Table 2 contains information about the number concentration and related reactive surface area. (The method to calculate the reactive surface area and mass size distribution of TiO₂ were presented in details in the supplementary materials).

Fig. 2. NO₂ photolysis frequency $j(\text{NO}_2)$ as a function of the number of UV lamps.

Fig. 3. Averaged normalized number size distribution of TiO₂ nanoparticles.

Table 2. Generated TiO₂ concentrations and corresponding reactive surface area.

TiO ₂ concentration (cm ⁻³)	0.47E+06	1.03E+06	1.72E+06	3.23E+06
Reactive surface area concentration (m ² m ⁻³)	0.102	0.38	0.79	2.86

2.5 Uptake Coefficient

Results are presented in two different formats: Fig. 4 presents the reduction of the NO₂ at the outlet of the reactor as a function of the UVA exposure for different TiO₂ reactive surface area concentrations. The results are further presented in terms of the uptake coefficient (γ) in Fig. 5. The uptake coefficient reflects both physical and chemical processes and represents the rate of effective collisions between TiO₂ nanoparticles and NO₂ gas molecules (Bartolomei *et al.*, 2014). The uptake coefficient as a dimensionless parameter, which considers the effect of exposure time and reactive surface effects on NO₂ reduction, is an appropriate number for reporting photochemical reaction and also for comparison with previous results. The uptake coefficient is calculated according to Eq. (5):

$$\gamma = \frac{4 \cdot k}{v \cdot A_s} \quad (5)$$

where k is the first-order reaction rate (s⁻¹), v is the mean molecular speed of NO₂ (m s⁻¹) and A_s (m² m⁻³) is the reactive surface area concentration. The first-order reaction rate, which is used to calculate the rate of NO₂, was calculated as follows:

$$k = -\frac{dc}{dt} \rightarrow k = \frac{1}{\Delta t} \ln \frac{c_0}{c_i} \quad (6)$$

where c_0 represents the NO₂ concentration in the absence and c_i in the presence of UVA light, each measured at the reactor outlet. Δt is the exposure time which is 29.2 s if only one group of lamps is active. If lamps from two groups are switched on, Δt is 58.4 s and with lamps from all three groups 87.6 s, respectively.

Fig. 4. NO₂ reduction as a function of UVA exposure for different TiO₂ reactive surface area concentrations.

Fig. 5. Uptake coefficient as a function of UVA exposure for different TiO₂ reactive surface area concentrations.

3 RESULTS AND DISCUSSION

3.1 Effect of TiO₂ Concentrations and UVA Exposure on the NO₂ Concentration

The reduction and uptake coefficient are presented in Figs. 4 and 5, respectively, for reactive surface area concentrations between 0.102 and 2.86 m² m⁻³, which were illuminated under UVA exposure in the range of 351.6–2109 W s m⁻² (one to six lamps from the first group with an exposure time of 29.2 s).

In the presence of TiO₂ nanoparticles, the NO₂ reduction gradually increases with increasing UVA exposure (the effect of UVA exposure on the photochemical reactions in the presence of

TiO₂ is presented in the supplementary materials in the section “The effect of UVA exposure on the photocatalysis reaction”). For instance, the reduction increased from 35.7% to 63.2% by increasing the UVA exposure from 351.6 W s m⁻² (one active lamp) to 2109 W s m⁻² (six active lamps) with a reactive surface area concentration of 0.79 m² m⁻³. This trend is in good agreement with previous studies. Bartolomei *et al.* (2014) showed that increasing light intensity as well as exposure time leads to a higher decrease of the NO₂ concentration. Our experimental results further show that with increasing reactive surface area concentration, the reduction also grew for each tested UVA exposure. For UVA exposure of 1055 W s m⁻² (three active lamps), the NO₂ reduction increased from 27.5% to 97.3% by enlarging the reactive surface area concentration from 0.102 to 2.86 m² m⁻³. (It is necessary to explain that the reported reduction of nearly 100% only applies to the experimental conditions used in the present experiment. The reduction depends on the NO₂ concentration, UVA exposure and reactive surface area concentration.) Zein and Bedjanian (2012) similarly reported that by increasing the surface length coated with TiO₂ in their experiment by a factor of 4, the ratio of the NO₂ concentration at the outlet to the inlet reduced by a factor of 3.

By increasing the reactive surface area, the dependency of NO₂ loss on UVA exposure decreased (chemical reactions and explanation related to the role of TiO₂ on the photochemical reactions are presented in the section “Governing photochemical reaction inside the reactor” in the supplementary materials). For example, for a reactive surface area concentration of 0.102 m² m⁻³, the reduction of NO₂ increased by a factor of 2.7 times by adding UVA exposure from 351.6 to 2109 W s m⁻². However, for the reactive surface area concentrations of 0.79 and 2.8 m² m⁻³ the NO₂ concentrations were reduced by a factor of 1.7 and 1, respectively, for the same range of UVA exposure. Our experimental results also show that for the highest UVA exposures, the reactive surface area concentration only plays a minor role. For instance, by changing the reactive surface from 0.102 to 2.8 m² m⁻³ the reduction increased by a factor of 7 for the UVA exposure of 351.6 W s m⁻². This increase was reduced to a factor of 1.75 for the UVA exposure of 6328 W s m⁻². (Results in details are presented in Table S1 in the supplementary materials.)

Fig. 5 shows the uptake coefficient as a function of UVA exposure for different TiO₂ reactive surface area concentrations. (The first-order reaction rate is calculated, and results are presented in Fig. S3.) The trend of the uptake coefficient, for each reactive surface area concentration, is increasing with increasing UVA exposure. For instance, the uptake coefficient raised from 4.9E-04 to 1.5E-03 by increasing the UVA exposure from 351.6 W s m⁻² (one active lamp) to 2109 W s m⁻² (six active lamps) with a reactive surface area concentration of 0.102 m² m⁻³. For a reactive surface area concentration of 0.79 m² m⁻³, an increase of the UVA exposure from 351.6 to 2109 W s m⁻² (6-fold) resulted in an increase of the uptake coefficient by a factor of 2.25. This result is in line with those reported by Zein and Bedjanian (2012). In their study, they also report that a 6-fold increase of the irradiation intensity (increasing $j = 0.002$ to 0.012 s⁻¹) increased the uptake coefficient by a factor of approximately 2.

Investigating the effect of TiO₂ reactive surface area concentration in our experiments showed that adding the TiO₂ nanoparticle concentration increases the photocatalytic reaction of NO₂ (Fig. 4) and consequently resulted in a higher reaction rate (Fig. S3). However, the trend of the uptake coefficient decreases with increasing TiO₂ reactive surface area concentration (more information is added to the section “The effect of TiO₂ on uptake coefficient” in the supplementary materials. The graph of uptake coefficient versus reactive surface area concentration (Fig. S4) is also presented that section.) Similar results were reported by Zein and Bedjanian (2012), who reported that the uptake coefficient decreased with increasing the TiO₂ mass over the illuminated surface. The upper limit of the uptake coefficient in their research was 1.9E-03 which was for the smallest TiO₂ mass for coating the reactive surface.

The highest uptake coefficient resulting from our experiments was 1.5E-03 for a reactive surface area concentration of 0.102 m² m⁻³ and a UVA exposure of 2109 W s m⁻² ($j = 0.012$ s⁻¹), while the lowest uptake coefficient was 2E-04 for a reactive surface area concentration of 0.79 m² m⁻³ and a UVA exposure of 361.5 W s m⁻² ($j = 0.002$ s⁻¹). This is again in good agreement with the results reported by Zein and Bedjanian (2012) who found uptake coefficients between 0.0019 and 0.00012 for 0.002 s⁻¹ $\leq j \leq 0.012$ s⁻¹. Gustaffson *et al.* (2006) also reported the range of uptake coefficient for aerosolized TiO₂ to be in the range between 1.2E-04 and 9.6E-04 for different relative humidity levels and with a reactive surface area concentration of 0.43 m² m⁻³. In summary,

the comparison of our data with those obtained by Gustaffson *et al.* (2006) and Zein and Bedjanian (2012) show that results from aerosolized TiO₂ nanoparticles compare well with those from TiO₂-coated surfaces when the Brunauer-Emmet-Teller (BET) surface area concentration, provided by the manufacturer, is used as the reactive surface area concentration in the data evaluation of the aerosol experiments. (The details of reduction, first-order reaction rate and uptake coefficient of reported results are presented in Table S1.)

3.2 Effect of Exposure Time on the NO₂ Reduction

To investigate the effect of exposure time on the reduction of the NO₂ concentration and the uptake coefficient, two different intensities of 12 W m⁻² (one lamp) and 72 W m⁻² (six lamps) for two reactive surface area concentrations of 0.102 and 0.79 m² m⁻³, are presented in Figs. 6 and 7, respectively. For the constant intensity of 12 W m⁻² (or 72 W m⁻²), the exposure time is 29.2 s for one lamp (or six lamps) in the first group. The exposure time of 58.4 and 87.6 s was adjusted by adding one lamp (or six lamps) in the second and third group, respectively. The arrangement of lamps is presented for one and six lamps in Figs. S5 and S6, respectively.

Fig. 6 shows that illumination of the reactor with a high intensity (72 W m⁻²) resulted in the highest reduction of the NO₂ concentration, but the effect of the exposure time gets weaker as an increase of the UVA exposure time by a factor of 3 only resulted in an approximately 30% higher decrease in the NO₂ reduction. For instance, by increasing the exposure time from 29.2 to 87.6 s with a reactive surface area concentration of 0.79 m² m⁻³, the reduction increases only by a factor of 1.26. In contrast, the enhancement of the reduction for the lower intensity is higher and showed a nearly linear trend. Comparison of results also revealed that for the longer exposure time the effect of UVA intensity is dominant compared to the effect of the reactive surface area. For instance, one can note that the difference between the NO₂ concentration reduction increased between two cases of reactive surface area concentration of 0.102 m² m⁻³ and UVA intensity of 72 W m⁻² and reactive surface area concentration of 0.79 m² m⁻³ and intensity of 12 W m⁻². For the same exposure time, the case of the nearly 8 times higher reactive surface area concentration resulted in a lower NO₂ reduction compared with the case of 6 times higher UVA exposure time. A similar trend was observed between two cases of “reactive surface area concentration of 0.102 m² m⁻³ and UVA intensity of 12 W m⁻²” and “without TiO₂ nanoparticles and UVA intensity of 72 W m⁻²” where the higher UVA intensity resulted in higher NO₂ reduction, even in absence of TiO₂ nanoparticles. (Results of first-order reaction rate are shown in Fig. S7.)

Fig. 6. Reduction of NO₂ concentration as function of exposure time for two reactive surface area concentrations (0.102 and 0.79 m² m⁻³) and two different UVA intensities (12 and 72 W m⁻²).

Fig. 7. Uptake coefficient versus exposure time for two different UVA intensities of 12 and 72 W m⁻² and reactive surfaces of 0.102 and 0.79 m² m⁻³.

Our results (Fig. 7) show that the uptake coefficient decreases by increasing the exposure time. A similar descending trend for the uptake coefficient versus exposure time has been reported in the literature (Laufs *et al.*, 2010; Zein and Bedjanian, 2012; Bartolomei *et al.*, 2014). According to Zein and Bedjanian (2012) this is caused by the fact that the experimental conditions approach steady state condition, in which the TiO₂ nanoparticles start to deactivate (more explanation is presented in the section “The effect of exposure time on the rate of NO₂ reduction” in the supplementary materials). Fig. 7 also shows that for each investigated exposure time, a higher intensity results in a higher uptake coefficient and thus a stronger photocatalytic reaction. Comparing the experimental results showed that the dependence of the uptake coefficient on UVA intensity is higher for lower reactive surface area concentrations. In the same way, the effect of reactive surface area concentration is dominant for low UVA intensity.

3.3 Effect of Humidity on the NO₂ Reduction

The effect of humidity on the reduction of NO₂ and uptake coefficients was investigated for relative humidity values of 5%, 35% and 70%. The NO₂ reduction and uptake coefficients under UVA exposure 351.6, 1055, and 6328 W s m⁻² for two different TiO₂ reactive surface area concentrations of 0.102 and 0.79 m² m⁻³ are presented in Fig. 8.

Figs. 8(a) and 8(b) show the reduction for the reactive surface area concentration of 0.102 and 0.79 m² m⁻³, respectively. For the lower reactive surface area concentration of 0.102 m² m⁻³, there is no clear difference between the relative humidity of 5% and 35%. However, by increasing the relative humidity from 35% to 70%, the reduction of the NO₂ concentration shows a slight increase. For the highest UVA exposure (6328 W s m⁻²), the effect of humidity is low and the dominant source of the NO₂ reduction is UVA exposure.

By increasing the reactive surface area concentration to 0.79 m² m⁻³ (Fig. 8(b)), the relative humidity also has an effect on the NO₂ reduction at low UVA exposure; however, for the high UVA exposure (6328 W s m⁻²), noticeable differences were not observed and the reduction of NO₂ for all three different relative humidity values were around 80%. The results for a reactive surface area concentration of 0.79 m² m⁻³ and lower UVA exposure are in general agreement with the findings of Bartolmie *et al.* (2014), who reported that the NO₂ reduction was higher at a relative humidity of 70% than at 50% for an exposure time up to 3.5 s and a UVA intensity of 10.6 W m⁻² over a coated surface. Zein and Bedjanian (2012) reported the initial first-order reaction rate to be higher at 40% relative humidity than at 0%. However, for long UVA exposure time, the

Fig. 8. Effect of relative humidity on the (a) NO₂ reduction for reactive surface area concentration of 0.102 m² m⁻³, (b) NO₂ reduction for reactive surface area concentration of 0.79 m² m⁻³, (c) NO₂ uptake coefficient for reactive surface area concentration of 0.102 m² m⁻³, and (d) NO₂ uptake coefficient for reactive surface area concentration of 0.79 m² m⁻³ as a function of UVA exposure.

difference was not noticeable anymore. (The first-order reaction rate for both reactive surface area concentrations of 0.102 and 0.79 m² m⁻³ are presented in Fig. S8.)

The uptake coefficient for the reactive surface area concentrations of 0.102 and 0.79 m² m⁻³ are presented in Figs. 8(c) and 8(d), respectively. For the lower UVA exposure (351.6 and 1055 W s m⁻², intensity of 12 and 36 W m⁻² and an exposure time of 29.2 s), the effect of increasing relative humidity is negligible for reactive surface area concentrations of 0.102 m² m⁻³ in comparison with 0.79 m² m⁻³, especially for low relative humidity levels (5–35%). In previous research (Pradhan *et al.*, 2010T; ang *et al.*, 2014), it was reported that the uptake coefficient is constant for relative humidity levels below 40%, since the amount of adsorbed water is quite low. However, for higher relative humidity, they reported an increasing trend for the uptake coefficient. They explained that increasing the water layer on the TiO₂ nanoparticle surface leads to an increase of the uptake coefficient (more details are presented in the section “The effect of humidity on uptake coefficient” in the supplementary materials). Our experimental results also show that the uptake coefficient

is increased at a relative humidity level of 70% for the reactive surface area concentrations of $0.102 \text{ m}^2 \text{ m}^{-3}$. In the case of reactive surface area concentration of $0.79 \text{ m}^2 \text{ m}^{-3}$, results showed an increasing trend with increasing relative humidity up to 40%. This difference is due to the relatively large reactive surface area, which made it possible to adsorb more water and thus leads to a higher uptake coefficient than at the low relative humidity level of 5%.

For the UVA exposure of 6328 W s m^{-2} (72 W m^{-2} with exposure time of 87.6 s), the explanation about exposure time is added in the supplementary materials; the uptake coefficient for all three relative humidity cases showed similar results for both reactive surfaces of 0.102 and $0.79 \text{ m}^2 \text{ m}^{-3}$. Zein and Bedjanian (2012) also reported that the uptake coefficient is not sensitive to relative humidity in the case of high exposure time which agrees with our results for the high UVA exposure. They reported that for NO_2 concentration of $10^{13} \text{ molecules cm}^{-3}$ (around 406.5 ppb) under UVA with photolysis frequency 0.006 s^{-1} (similar to two lamps in our study, 24 W m^{-2}) with TiO_2 sample mass of 0.4 mg cm^{-1} ($2320 \text{ m}^2 \text{ m}^{-3}$, by considering TiO_2 density with 1.236 g cm^{-3} and tube diameter of 2.4 cm). For our experimental condition, the amount of intensity is 9 times higher and the amount of reactive surface is around 2937 times lower than Zein and Bedjanian (2012) experiment conditions. Therefore, it can be expected that the speed of approaching TiO_2 nanoparticles to steady state condition, in our experimental condition, occurred quite faster. Gustaffson *et al.* (2006) investigated the reaction between NO_2 (with mixing ratio of 100 ppbv) and aerosolized TiO_2 (with the concentration of $0.43 \text{ m}^2 \text{ m}^{-3}$) under UVA illumination with the intensity of 16 W m^{-2} for relative humidity levels between 15% and 80%. They reported the lower and upper limit to be $1.2\text{E-}04$ and $9.6\text{E-}04$, respectively, which is in good agreement with our results (between $1.9\text{E-}04$ and $1.5\text{E-}03$). However, the results presented by Gustaffson *et al.* (2006) showed a negative correlation with relative humidity which is different from our results as well as results reported by Zein and Bedjanian (2012) and Bartolmie *et al.* (2014). Zein and Bedjanian (2012) explained this difference to be possibly due to the short exposure time. The different results obtained by Gustaffson *et al.* (2006) cannot be explained at this point, because their paper does not provide information on the flow rate, exposure time and geometry of their experimental set-up.

4 CONCLUSION

We investigated the reduction of NO_2 using aerosolized TiO_2 nanoparticles, which ranged from 0.102 to $2.8 \text{ m}^2 \text{ m}^{-3}$ in reactive surface area concentration (and from $0.47\text{E}+06$ to $3.23\text{E}+06 \text{ cm}^{-3}$ in number concentration, respectively), and UVA, which ranged from 351.6 to 6328 W s m^{-2} . In general, the UVA alone caused the largest decrease in the ambient NO_2 . Only high concentrations of TiO_2 produced a noticeable effect ($> 0.102 \text{ m}^2 \text{ m}^{-3}$ [$> 0.47\text{E}+06 \text{ cm}^{-3}$]), although the maximum value ($2.8 \text{ m}^2 \text{ m}^{-3}$ [$3.23 \text{ E} + 06 \text{ cm}^{-3}$]) drove a reduction in the NO_2 that was almost dissociated from the UV intensity when the exposure was continuous. Thus, we established that the drop in NO_2 depended on both the TiO_2 concentration and the UV exposure when the former was high. The upper limit of the uptake coefficient was $1.5\text{E-}03$ when the reactive surface area concentration was $0.102 \text{ m}^2 \text{ m}^{-3}$ and the UVA exposure was 6328 W s m^{-2} , and the lower limit was $1.9\text{E-}04$ when the concentration was $0.79 \text{ m}^2 \text{ m}^{-3}$ and the exposure was 351.6 W s m^{-2} . Moreover, we discovered that the percentage of reduction attributable to the UVA intensity grew with the exposure time, possibly owing to the deactivation of the TiO_2 .

Finally, we also assessed the effect of the relative humidity on the NO_2 reduction under varying conditions. The influence of this factor, although significant when the UVA intensity and the TiO_2 concentration were high and low, respectively, became negligible when the UVA intensity was high, regardless of the TiO_2 concentration.

ACKNOWLEDGEMENT

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme (Grant Agreement No. 646002) as part of the NanoFASE project.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.200612>

REFERENCES

- Augustynski, J. (1993). The role of the surface intermediates in the photoelectrochemical behaviour of anatase and rutile TiO₂. *Electrochim. Acta* 38, 43–46. [https://doi.org/10.1016/0013-4686\(93\)80008-N](https://doi.org/10.1016/0013-4686(93)80008-N)
- Ballari, M.M., Yu, Q.L., Brouwers, H.J.H. (2011). Experimental study of the NO and NO₂ degradation by photocatalytically active concrete. *Catal. Today* 161, 175–180. <https://doi.org/10.1016/j.cattod.2010.09.028>
- Bartolomei, V., Sörgel, M., Gligorovski, S., Alvarez, E.G., Gandolfo, A., Strekowski, R., Quivet, E., Held, A., Zetzsch, C., Wortham, H. (2014). Formation of indoor nitrous acid (HONO) by light-induced NO₂ heterogeneous reactions with white wall paint. *Environ. Sci. Pollut. Res.* 21, 9259–9269. <https://doi.org/10.1007/s11356-014-2836-5>
- Bohn, B., Rohrer, F., Brauers, T., Wahner, A. (2005). Actinometric measurements of NO₂ photolysis frequencies in the atmosphere simulation chamber SAPHIR. *Atmos. Chem. Phys.* 5, 493–503. <https://doi.org/10.1007/s11356-014-2836-5>
- Chen, H., Nanayakkara, C.E., Grassian, V.H. (2012). Titanium dioxide photocatalysis in atmospheric chemistry. *Chem. Rev.* 112, 5919. <https://doi.org/10.1021/cr3002092>
- Chen, J., Li, G., Zhang, H., Liu, P., Zhao, H., An, T. (2014). Anatase TiO₂ mesocrystals with exposed (0 0 1) surface for enhanced photocatalytic decomposition capability toward gaseous styrene. *Catal. Today* 224, 216. <https://doi.org/10.1016/j.cattod.2013.10.073>
- Dalton, J.S., Janes, P.A., Jones, N.G., Nicholson, J.A., Hallam, K.R., Allen, G.C. (2002). Photocatalytic oxidation of NO_x gases using TiO₂: A surface spectroscopic approach. *Environ. Pollut.* 120, 415. [https://doi.org/10.1016/S0269-7491\(02\)00107-0](https://doi.org/10.1016/S0269-7491(02)00107-0)
- Devahasdin, S., Fan, C., Jr, Li, K., Chen, D.H. (2003). TiO₂ photocatalytic oxidation of nitric oxide: Transient behavior and reaction kinetics. *J. Photochem. Photobiol., A* 156, 161–170. [https://doi.org/10.1016/S1010-6030\(03\)00005-4](https://doi.org/10.1016/S1010-6030(03)00005-4)
- European Environment Agency (EEA) (2020) Air quality in Europe — 2020 report. <https://www.eea.europa.eu/publications/air-quality-in-europe-2020-report> (accessed 23. November 2020).
- Febo, A., Perrino, C., Cortiello, M. (1993). A denuder technique for the measurement of nitrous acid in urban atmospheres. *Atmos. Environ.* 27, 1721–1728. [https://doi.org/10.1016/0960-1686\(93\)90235-Q](https://doi.org/10.1016/0960-1686(93)90235-Q)
- Febo, A., Perrino, C., Gherardi, M., Sparapani, R. (1995). Evaluation of a high-purity and high-stability continuous generation system for nitrous acid. *Environ. Sci. Technol.* 29, 2390–2395. <https://doi.org/10.1021/es00009a035>
- Fujishima, A., Zhang, X., Tryk, D.A. (2008). TiO₂ photocatalysis and related surface phenomena. *Surf. Sci. Rep.* 63, 515. <https://doi.org/10.1016/j.surfrep.2008.10.001>
- Gottschalk, F., Nowack, B. (2011). The release of engineered nanomaterials to the environment. *J. Environ. Monit.* 13, 1145–1155. <https://doi.org/10.1039/C0EM00547A>
- Gustafsson, R.J., Orlov, A., Griffiths, P.T., Cox, R.A., Lambert, R.M. (2006). Reduction of NO₂ to nitrous acid on illuminated titanium dioxide aerosol surfaces: Implications for photocatalysis and atmospheric chemistry. *Chem. Commun.* 3936–3938. <https://doi.org/10.1039/B609005B>
- Hessisches Landesamt für Naturschutz, Umwelt und Geologie. <https://www.hlnug.de/themen/luft.html.%20Zugegriffen> Zugegriffen: 07. Sept. 2017.
- John, A.C., Küpper, M., Manders-Groot, A.M., Debray, B., Lacome, J.M., Kuhlbusch, T.A. (2017). Emissions and possible environmental implication of engineered nanomaterials (ENMs) in the atmosphere. *Atmosphere* 8, 84. <https://doi.org/10.3390/atmos8050084>
- Kampa, M., Castanas, E. (2008). Human health effects of air pollution. *Environ. Pollut.* 151, 362–367. <https://doi.org/10.1016/j.envpol.2007.06.012>
- Kebede, M.A., Varner, M.E., Scharko, N.K., Gerber, R.B., Raff, J.D. (2013). Photooxidation of Ammonia on TiO₂ as a Source of NO and NO₂ under Atmospheric Conditions. *J. Am. Chem. Soc.*

- 135, 8606–8615. <https://doi.org/10.1021/ja401846x>
- Keller, A., McFerran, S., Lazareva, A., Suh, S. (2013). Global life cycle releases of engineered nanomaterials. *J. Nanopart. Res.* 15, 1. <https://doi.org/10.1007/s11051-013-1692-4>
- Langridge, J.M., Gustafsson, R.J., Griffiths, P.T., Cox, R.A., Lambert, R.M., Jones, R.L. (2009). Solar driven nitrous acid formation on building material surfaces containing titanium dioxide: A concern for air quality in urban areas? *Atmos. Environ.* 43, 5128–5131. <https://doi.org/10.1016/j.atmosenv.2009.06.046>
- Laufs, S., Burgeth, G., Duttlinger, W., Kurtenbach, R., Maban, M., Thomas, C., Wiesen, P., Kleffmann, J. (2010). Conversion of nitrogen oxides on commercial photocatalytic dispersion paints. *Atmos. Environ.* 44, 2341–2349. <https://doi.org/10.1016/j.atmosenv.2010.03.038>
- Lin, H., Huang, C.P., Li, W., Ni, C., Shah, S.I., Tseng, Y.H. (2006). Size dependency of nanocrystalline TiO₂ on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol. *Appl. Catal., B* 68, 1–11. <https://doi.org/10.1016/j.apcatb.2006.07.018>
- Maggos, T., Bartzis, J.G., Leva, P., Kotzias, D. (2007). Application of photocatalytic technology for NO_x removal. *Appl. Phys. A* 89, 81–84. <https://doi.org/10.1007/s00339-007-4033-6>
- Monge, M.E., D'Anna, B., George, C. (2010). Nitrogen dioxide removal and nitrous acid formation on titanium oxide surfaces—An air quality remediation process? *Phys. Chem. Chem. Phys.* 12, 8991–8998. <https://doi.org/10.1039/B925785C>
- Mueller, N.C., Nowack, B. (2008) Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* 42, 4447. <https://doi.org/10.1021/es7029637>
- Ohko, Y., Nakamura, Y., Fukuda, A., Matsuzawa, S., Takeuchi, K. (2008). Photocatalytic oxidation of nitrogen dioxide with TiO₂ thin films under continuous UV-light illumination. *J. Phys. Chem. C* 112, 10502–10508. <https://doi.org/10.1021/jp802959c>
- Piccinno, F., Gottschalk, F., Seeger, S., Nowack, B. (2012). Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *J. Nanopart. Res.* 14, 1109. <https://doi.org/10.1007/s11051-012-1109-9>
- Pradhan, M., Kyriakou, G., Archibald, A.T., Papageorgiou, A.C., Kalberer, M., Lambert, R.M. (2010). Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: A potential missing sink for H₂O₂ in the troposphere. *Atmos. Chem. Phys.* 10, 7127. <https://doi.org/10.5194/acp-10-7127-2010>
- Tang, M.J., Telford, P.J., Pope, F.D., Rkiouak, L., Abraham, N.L., Archibald, A.T., Braesicke, P., Pyle, J.A., McGregor, J., Watson, I.M., Cox, R.A., Kalberer, M. (2014). Heterogeneous reaction of N₂O₅ with airborne TiO₂ particles and its implication for stratospheric particle injection. *Atmos. Chem. Phys.* 14, 6035–6048. <https://doi.org/10.5194/acp-14-6035-2014>
- Tobaldi, D. M., Pullar, R.C., Seabra, M.P., Labrincha, J.A. (2014). Fully quantitative X-ray characterisation of Evonik Aeroxide TiO₂ P25®. *Mater. Lett.* 122, 345–347. <https://doi.org/10.1016/j.matlet.2014.02.055>
- Uekawa, N., Suzuki, M., Ohmiya, T., Mori, F., Wu, Y.J., Kakegawa, K. (2003). Synthesis of rutile and anatase TiO₂ nanoparticles from Ti-peroxy compound aqueous solution with polyols. *J. Mater. Res.* 18, 797–803. <https://doi.org/10.1557/JMR.2003.0110>
- Volz-Thomas, A., Beekmann, M., Derwent, D., Law, K., Lindskog, A., Prévôt, A., ... & Stohl, A. (2003). Towards Cleaner Air for Europe-Science, Tools, and Applications part 1: Results from the EUROTRAC-2 Synthesis and Integration Project. *Markgraf*.
- Yusoff, R., Kathawala, M.H., Nguyen, L.T.H., Setyawati, M.I., Chiew, P., Wu, Y., Ch'ng, A.L., Wang, Z.M., Ng, K.W. (2018). Biomolecular interaction and kinematics differences between P25 and E171 TiO₂ nanoparticles. *NanoImpact* 12, 51–57. <https://doi.org/10.1016/j.impact.2018.10.001>
- Zein, A.E., Bedjanian, Y. (2012). Interaction of NO₂ with TiO₂ surface under UV irradiation: Measurements of the uptake coefficient. *Atmos. Chem. Phys.* 12, 1013–1020. <https://doi.org/10.5194/acp-12-1013-2012>