UNIVERSITY OF LEEDS

This is a repository copy of Influence of TiO2-based photocatalytic coating road on trafficrelated NOx pollutants in urban street canyon by CFD modeling.

White Rose Research Online URL for this paper: <u>https://eprints.whiterose.ac.uk/161108/</u>

Version: Accepted Version

Article:

Xie, X, Hao, C, Huang, Y orcid.org/0000-0002-1220-6896 et al. (1 more author) (2020) Influence of TiO2-based photocatalytic coating road on traffic-related NOx pollutants in urban street canyon by CFD modeling. Science of The Total Environment, 724. 138059. ISSN 0048-9697

https://doi.org/10.1016/j.scitotenv.2020.138059

© 2020 Elsevier B.V. All rights reserved. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/

1	Influence of TiO ₂ -based photocatalytic coating road on traffic-related
2	NO _x pollutants in urban street canyon by CFD modeling
3	Xiaomin Xie*1, Chenrui Hao1, Yue Huang2, Zhen Huang1,
4	1 Key Laboratory for Power machinery and Engineering of M. O. E., Shanghai Jiao
5	Tong University, No. 800, Dongchuan Road, 200240 Shanghai, P R China
6	2 Institute for Transport Studies, University of Leeds, 34-40 University Road, Leeds,
7	LS2 9JT, UK
8	
9	ABSTRACT
10	The use of titanium dioxide (TiO ₂) photocatalytic nanoparticles as road coating to trap
11	and decompose air pollutants provides a promising technology to mitigate the harmful
12	effects of vehicle emissions. However, there are few studies on computational fluid
13	dynamics (CFD) simulations of the effect of NOx photocatalytic oxidation in street
14	canyon with TiO_2 nanoparticles as pavement coating. This study developed a CFD
15	model with photocatalytic oxidation (PCO) reaction implemented for numerical
16	simulation of NO _x abatement in an urban street canyon with TiO_2 coating, considering
17	the effects of relative humidity (<i>RH</i>) (10–90%) and irradiance (10–40 $W \cdot m^{-2}$). Results
18	show that TiO_2 coating road can effectively reduce nitrogen oxide (NO _x) concentration
19	in the street canyon. The average nitric oxide (NO) and nitrogen dioxide (NO ₂)
20	concentrations in street canyon with TiO_2 coating road were reduced by 3.70% and
21	4.31%, respectively, comparing with street canyon without TiO_2 coating. The irradiance

22 and relative humidity had great effect on PCO reaction in street canyon with TiO₂ coating road. When the irradiance increased from $10W \cdot m^{-2}$ to $40W \cdot m^{-2}$, average NO 23 conversion rose from 1.35% to 3.70%, and average NO₂ conversion rose from 2.43% 24 25 to 4.31%. The average conversion of NO and NO₂ decreased from 5.11% to 2.54% and from 5.60% to 3.25%, respectively, when the relative humidity varied from 10% to 90%. 26 27 Results are useful to transport planners and road engineers who need to reduce NOx 28 concentrations in urban streets travelled by fossil fuel-powered vehicles. Method of the 29 study can be considered by future research faced with different pavement construction 30 and traffic environment.

31 Keywords: Street canyon; TiO₂ coating road; NO_x concentration; photocatalytic
32 oxidation (PCO); computational fluid dynamics (CFD) simulation

33

34 1. Introduction

The total NO_x emissions were 12.59 Mt in China in 2017 (National Bureau of Statistics of China, 2019). Vehicle exhaust is a major contributor to NO_x emissions in cities with the rapidly growing automobile industry and urbanization. These activities yielded an increase of 1.4 Mt NOx in 2017 compared with the 2010 levels, while pollution control measures have yielded reductions of 1.3 Mt NO_x (Zheng et al., 2018). In 2017, NO_x emissions from vehicles were estimated to be 5.74 Mt (National Ministry of Ecology and Environment of China, 2018), accounting for 45.6% of the total NO_x

42	emissions in China. $\ensuremath{\mathrm{NO}_x}$ cause a wide range of environmental issues, such as the
43	formation of tropospheric ozone and urban smog through photochemical reactions with
44	hydrocarbons. Furthermore, NO_x can cause acute respiratory tract infections and
45	cardiovascular diseases (Notario et al., 2012). Road pavement, in initial and direct
46	contact with tailpipe emissions, provides an opportunity to retain and convert the
47	pollutants to less harmful substances. Photocatalytic oxidation (PCO) is found effective
48	in reducing air pollution caused by NOx. PCO using TiO_2 has drawn public attention
49	for air quality reasons with their advantages of high oxidation efficiency, innocuity and
50	low cost (Jiang et al., 2019).

51 Photocatalytic concrete coated with TiO₂ are widely experimented (Devahasdin et al., 2003; Faraldos et al., 2016). Lasek et al. (2013) summarized the oxidation 52 53 mechanism, various processes and conditions of PCO for NO_x removal. Mothes et al. 54 (2018) assessed the photocatalytic performance of cement-based materials containing 55 TiO₂ for NO_x reduction, by determining the kinetic parameters under various 56 experimental conditions (relative humidity, flow rate, mixing ratio and light intensity) 57 in small-scale bed flow photoreactor experiments. Some key physic-chemical factors influencing the effectiveness of photocatalytic concrete are tested in experiments by 58 59 (Macphee and Folli, 2016; Yang et al., 2019) on a micro level. Mendoza et al. (2017) 60 investigated the effectiveness of surface modified by WO₃/TiO₂ (WO₃, tungsten 61 trioxide) composite particles in removing gaseous NO_x under visible light irradiation. Study by Guo et al. (2017) was focusing on the method of applying nano-TiO₂ to 62

concrete surface. Based on Langmuir-Hinshelwood kinetics equation, the PCO reaction
rate was modelled in experiments (Ballari et al., 2010). In other experiments, the
reaction rate was fixed considering relative humidity and irradiance (Devahasdin et al.,
2003; Lira et al., 2018; Yu et al., 2010).

67 In addition to concrete, experiments were also carried out on asphalt pavement (Chen 68 and Chu, 2011)(Folli et al., 2015). De Melo et al. (2012) tested road pavement overlaid 69 with cement mortar which contains varying levels of TiO₂ (3%, 6% and 10%) for their 70 photocatalytic efficiency. Results indicated that higher TiO₂ contents in a porous 71 pavement surface are more efficient in the degradation of NOx. Fan et al. (2018) 72 developed a solar photocatalytic asphalt for removing vehicular NOx and mitigating 73 roadside air pollution problem by chamber tests and field tests, who studied material 74 characterizations and evaluated the durability of the photocatalytic coating.

75 The use of TiO₂ photocatalytic nanoparticles as a road coating to trap and 76 decompose air pollutants provides a promising technology to mitigate the harmful 77 effects of vehicle emissions. Certain types of urban street layouts are known to be 78 detrimental to the dispersion of contaminants. One of the typical configurations for 79 gathering pollutants and causing harm to humans is the so-called street canyon, which means a street flanked by continuous buildings on both sides. Investigations on the 80 81 characteristics of vehicle emissions dispersion in street canyon with TiO₂ photocatalytic 82 nanoparticles as pavement coating are very important for further understanding the impact of TiO₂ photocatalytic nanoparticles pavement coating on the air quality in 83

84 urban environment.

Computational fluid dynamics (CFD) simulation is used to predict the dispersion 85 86 of reactive air pollutants within a street canyon, because it is quick and cost effective 87 comparing with photoreactor experiment and field measurements. Baker et al. (2004) 88 and Kikumoto and Ooka (2012) simulated the dispersion and transport of reactive air 89 pollutants (NO, NO₂ and O₃) in an urban street canyon using an LES model. Kwak et 90 al. (2013) conducted numerical simulations with a Reynolds Averaged Naviere Stokes 91 equation (RANS) model to analyze the impact of bottom heating in street canyons on 92 the flow and transport of reactive air pollutants (NO, NO₂ and O₃). Heat intensity, inflow wind and vegetation were found important factors that effect on reactive 93 94 pollution dispersion in urban street canyon (Xie and Zhu, 2018) (Moradpour et al., 95 2017). CFD techniques are effective tools for the simulation of reactive flow within 96 photocatalytic devices considering all the coupled phenomena taking place (Lira et al., 97 2018). CFD has been used to model flat plate photo reactor (Passalía et al., 2011) (Salvado, 2007) (Salvado and Hargreaves, 2007), multi-tube reactor (Jelle Roegiers, 98 99 2018) (Alpert et al., 2010), impeller reactor (Tokode et al., 2017) and rectangular reactor 100 (Einaga et al., 2015). The effects of film thickness (Vezzoli et al., 2013) and gas flow 101 rate (Alpert et al., 2010) (Einaga et al., 2015) have also been investigated. However, there are few studies on CFD simulations of the effect of NOx photocatalytic oxidation 102 103 in street canyon with TiO₂ photocatalytic nanoparticles as pavement coating. This paper aims to develop a coupled CFD-PCO model and investigate the effects of 104

105 TiO₂-based photocatalytic road coating on the NOx reduction in urban street canyon. 106 Furthermore, a comprehensive analysis of the key factors influencing the effectiveness 107 of the TiO₂-based photocatalytic coating road is carried out. Methodology in this study 108 will provide a fast and effective way for the investigation of the PCO reaction in street 109 canyon with TiO₂ coating road. Findings from this study shall be useful to road design 110 and transport planning to reduce reactive pollutant levels in urban traffic environment.

111 **2. Methodology**

112 **2.1 Flow modeling**

113 Computational fluid dynamics (CFD) modelling is based on numerical solutions to 114 derive dispersion equations and fluid flow simulation. These solutions are derived from 115 the principles of conservation and transmission. The air in street canyons can be 116 considered incompressible turbulent inert flow, and the density of air and pollutant is 117 assumed to be constant. As Sini et al. (1996) pointed out, these assumptions are 118 reasonable for most low-level atmospheric environments.

119 Steady RANS model has been widely used because its effectiveness in predicting 120 average airflows. Re-normalization group (RNG) $k - \varepsilon$ model is used in this study 121 according to previous research on the influence of structures on particulate matter 122 dispersion in street canyons by CFD modeling (Hao et al. 2019).

123 The commercial CFD software Fluent (Fluent, 2009) is used to implement the124 mathematical model above. Meanwhile, the governing equations are discretized using

the finite volume method and the second order upwind scheme. The SIMPLE schemeis used for the pressure and velocity coupling.

127 The inlet flow velocity is:

128
$$u(z) = U_0 (\frac{y - H}{Y})^{\alpha}$$
 (1)

129 where U_0 is the wind speed at the boundary, it is set as $U_0 = 3 \text{ m-s}^{-1}$. *H* is the height 130 of the building and *Y* is the thickness of the boundary which is set to 80 m in the paper. 131 The same thickness was also applied in Ai and Mak's simulation (Ai and Mak, 2017). 132 α is the wind profile exponent indicating the base surface roughness in relation to the

133 terrain category of mid-dense urban area, and was set to 0.22 (Hang et al., 2017).

134 Simulations in this study are performed with a full-scaled model. Fig.1 shows the computational domain. The buildings' height H and street's width W are all 20 m. The 135 136 ratio H/W = 1. Pollution inlet is set in the middle of the ground with 1 m wide. The 137 domain size is 20 m by 100 m in x and y directions. Regular grids of 0.1 m by 0.1 m 138 are applied to the whole area inside the street canyon. Grid size outside the canyon 139 increases as they have less effect. Velocity-inlet is applied to the air inlet. The outlet is 140 set with outflow condition. The top domain is considered symmetrical. Walls are 141 defined as non-slip walls. Temperature is set as 298K (about 25°C) in the domain and 142 at all the walls, which means the canyons are isothermal.

7



143

144

Fig.1. Computational domain

145 **2.2 PCO reaction mechanism**

146 A simplified photochemical steady state (PSS) O_3/NO_x model is implemented if the 147 road is without TiO2 coating. The chemical reactions considered are (Baik et al., 2007;

148 Carpenter et al., 1998)

149
$$NO_2 \xrightarrow{h\nu} NO + O^*, \quad R_1 = k_1 C_{NO_2}$$
 (2)

150
$$O^* + O_2 + M \longrightarrow O_3 + M$$
, $R_2 = k_2 C_{O^*} C_{O_2} C_M$ (3)

151
$$O_3 + NO \longrightarrow NO_2 + O_2, \quad R_3 = k_3 C_{O_3} C_{NO}$$
 (4)

In Eq.(2), hv represents photovoltaic processes triggered by sunlight. In Eq. (3),
M means a third-body molecule that absorbs energy and stabilizes O₃. Above reaction
mechanism has been widely used in previous studies (García-yee et al., 2018; Han et

155 al., 2018; Muilwijk et al., 2016; Ryerson et al., 2000; Xie and Zhu, 2018).

156 The rate of Eq. (2) is considered infinitely fast compared to the photolysis rate R_1 , e.g. $k_2 \approx \infty$ (Muilwijk et al., 2016). k_1 is specified as 0.0081 s⁻¹ and 157 $k_3 = 44.05 \times 10^{-3} exp(-1370/T) ppb^{-1}s^{-1}$ (Baik et al., 2007; Seinfeld, 2007). Eq. 2-4 are 158 combined with the steady RANS method to simulate the dispersion of NO and NO₂. 159 160 In this simulation, NO and NO₂ are released from the pollution inlet (Fig.1) with a mole fraction of 50 ppm and 5 ppm, respectively. The releasing speed is defined as 161 162 0.002m/s. It corresponds to about 1000 vehicles per hour, the emission intensity of NO and NO₂ are 120.7 $\mu g \Box m^{-1} s^{-1}$ and 18.5 $\mu g \Box m^{-1} s^{-1}$, respectively, assuming the NO_x 163 164 emission rate is 0.5 $g\Box km / s$ per vehicle (Baker et al., 2004). 165 Furthermore, road with nanometer TiO2 coating is associated with the photocatalytic 166 oxidation (PCO) of nitrogen oxides in street canyon. The related reactions are written 167 below (Allen et al., 2003): $TiO_2 + hv \longrightarrow TiO_2(e^- + h^+)$ 168 (5) $O_2 + e^- \longrightarrow O_2^{\square}$ 169 (6) $H_2O + h^+ \longrightarrow H^+ + HO^{\square}$ 170 (7) $NO + HO^{\Box} \longrightarrow HNO_{2}$ 171 (8)

$$172 \quad HNO_2 + HO^{\Box} \longrightarrow NO_2 + H_2O \tag{9}$$

$$173 \qquad NO_2 + HO^{\Box} \longrightarrow NO_3^- + H^+ \tag{10}$$

The Langmuir-Hinshelwood model has been widely used to model the reaction rate
for PCO (M. M. Ballari et al., 2010; Mills and Hunte, 1997; Muñoz et al., 2019). Ballari

et al. (2010) developed equations to calculate the reaction rate of NO and NO₂ for
surface reactions at constant *RH* and irradiance. Lira et al. (2018) took the effects of

178 *RH* and irradiance into account in developing the equations, which are written below:

179
$$r_{NO} = -\frac{k_{NO}C_{NO}}{1 + K_{NO}C_{NO} + K_{NO_2}C_{NO_2} + K_wC_w} (-1 + \sqrt{1 + \alpha E})$$
(11)

180
$$r_{NO_2} = -\frac{k_{NO_2} C_{NO_2} - k_{NO} C_{NO}}{1 + K_{NO} C_{NO} + K_{NO_2} C_{NO_2} + K_w C_w} (-1 + \sqrt{1 + \alpha E})$$
(12)

181 where $k_i^{'}$ and K_i are intrinsic kinetic and equilibrium parameters, respectively. α 182 is kinetic parameter related to irradiance and *E* is irradiance. The constants derived by 183 Lira et al. (2018) are based on the values derived by Ballari et al. (2010), which are 184 taken as reference values in this study. The values are listed in Table 2.

185

Table 2 Values adopted in Eq. (11-12) (Lira et al., 2018)

Parameter	Value	Unit
k_{NO}	4.18	$m \cdot s^{-1}$
$k_{\scriptscriptstyle NO_2}^{'}$	6.73	$m \cdot s^{-1}$
$K_{\scriptscriptstyle NO}$	8.48×10^{8}	$m^3 \cdot kmol^{-1}$
K_{NO_2}	3.02×10^{8}	$m^3 \cdot kmol^{-1}$
$K_{_W}$	5.07×10^{4}	$m^3 \cdot kmol^{-1}$
α	2.37×10 ⁻³	$m^2 \cdot W^{-1}$

Photoactive components of photocatalytic coatings are activated by ultraviolet (UV)
light (de Melo and Trichês, 2012)(Guo et al., 2017)(Diamanti et al., 2013). The
proportion of UV light to total radiation intensity is about 8.7% (Zhang, 2014).

189 According to the radiation intensity and RH data in different region of China (National

Bureau of Statistics of China, 2019), irradiance (*E*) varies in the range of 10-40 $W \cdot m^{-2}$,

191 *RH* varies in the range of 10%-90%. *E* of 40 $W \cdot m^{-2}$ and *RH* of 50% are set as the

192 reference condition in this study.

193 **2.3 Calculation for pollutant conversion**

194 In order to evaluate the effects of TiO_2 coating on the PCO reactions in street 195 canyon, pollutant conversion (X_{NO}) is defined as:

196
$$X_{i} = \left(\frac{C_{i}^{noPCO} - C_{i}^{PCO}}{C_{i}^{noPCO}}\right) \times 100\%$$
(13)

197 *i* stands for the type of the pollutant, here refer to NO and NO₂. C_i^{PCO} means the 198 average pollutant concentration using the model with PCO reactions. C_i^{noPCO} means 199 the average pollutant concentration using the model without PCO reactions. The higher 200 the X_i , the more effective the PCO reaction is.

201 3. Model validation

The accuracy of the above developed CFD model was evaluated using results from the wind-tunnel experiments by Allegrini et al. (2014). The validation setups for flow modeling have been detailed in previous publication (Hao et al., 2019). In order to validate the chemical reaction model, a 2D computational domain (Fig.2) with a length $(L+L^2)$ of 0.4 m and a height (*H*) of 3 mm was built similar to Lira et al.'s study (Lira et al., 2018) for comparing with Ballari et al.'s experiment (M. M. Ballari et al., 2010).

208	The domain's height uses value 2H and 4H (keeping the length constant). The bottom
209	of the domain with length L (0 < x < 0.2 m) is set as a reactive surface. The reaction
210	mechanism is written in Eq. (5-10). Domain with length L' ($0 < x < 0.2$ m) is set as a
211	control group without PCO to obtain a fully developed laminar velocity profile at x=0.
212	Inlet velocity is set to 0.1667 m/s. A concentration of $4.47 \times 10^{-8} kmol \cdot m^{-3}$ for NO and
213	a relative humidity of 50% is set at the inlet. A homogeneous irradiance of 10 $W \cdot m^{-2}$
214	is imposed at the reactive surface. Simulation results are compared to those from Lira
215	et al.'s (Lira et al., 2018) and Ballari et al.'s experiment (M. M. Ballari et al., 2010). In
216	order to compare the experiment results between different tests, the NO conversion
217	(X _{NO}) is specified as:

218
$$X_{NO} = \left(\frac{C_{NO}^{in} - C_{NO}^{avg,out}}{C_{NO}^{in}}\right) \times 100\%$$
(14)
Wind direction
219

Fig.2. Computational domain for chemical reaction validation

The results including comparison with those by Lira et al. (Lira et al., 2018) are shown in Fig.3. Fig.3(a) shows the reaction rates for NO along x-axis at the reactive surface. A gap was observed when comparing the results with Lira et al.'s. However, the tendency is the same that the rates decrease along the direction of wind. The reaction rates obtained in this study are lower than in the reference study. As a result, the profiles of NO mass fractions obtained for $0 \le x \le L$ (Fig.3(c)) in this study are higher than Lira et al.'s. The results for NO₂ are shown in Fig.3(b) & (d). Reaction rates of NO₂ at the reactive surface show high similarity with the reference. Values of NO₂ mass fractions
are higher in this study, compared to the reference.

Results for X_{NO} in this validation comparing with reference simulation (Lira et al., 2018) and experiment (M. M. Ballari et al., 2010) are shown in Fig.4. Clearly, there is a tendency of decreasing X_{NO} as the relative humidity increases. It is worth noting that simulation in this validation matches Ballari et al.'s experiment better than Lira et al.'s study (Lira et al., 2018), although it overestimates NO conversion. After validation, the chemical mechanism model applied in this study is considered reliable for predicting the chemical reaction and transformation.





(a) Reaction rates for NO along x-axis at



the reactive surface.

(b) Reaction rates for NO₂ along x-axis

at the reactive surface.



13

(c) Profiles of NO mass fractions

(d) Profiles of NO₂ mass fractions

obtained for $0 \le x \le L$ at y = 0.00, 0.0015

obtained for 0<x<L at y= 0.00, 0.0015

and 0.003 m

and 0.003 m

Fig.3. Comparison results with Lira et al.



Fig.4. Comparison of NO conversion (X_{NO}) with experiment as a function of

relative humidity

237 4. Results and discussion

4.1 NO_x dispersion in street canyon with TiO₂ coating road

239 In this section, simulation results of a street canyon with TiO_2 coating road are

240 compared with a street canyon without TiO₂ coating road.

Fig.5 illustrates the wind flow structures and pollutant dispersion patterns in the street

242 canyons with and without TiO₂ coating road. Due to the presence of clockwise eddy,

- 243 most of the pollutants accumulated in the leeward side, as shown in Fig.5a and Fig.5b.
- 244 Decreases of NO concentration were observed in the street canyon with TiO₂ coating
- road. In details, the average concentration of NO inside the street canyon with TiO₂

coating road is 6.06 ppm, while it is 6.29 ppm inside the street canyon without TiO_2 coating road, as shown in Fig.5c and Fig.5d. This means the average NO concentration decreases by 3.70% under the influence of PCO reactions. Similar reduction in NO₂ concentration inside the canyon is shown in Fig.5e and Fig.5f. The PCO decreases the average concentration of NO₂ by 4.31%.



(a) Flow filed and velocity contour in canyon without TiO₂ coating road.



(c) Contour of NO concentration in canyon without TiO₂ coating road.



(b) Flow filed and velocity contour in canyon with TiO₂ coating road.



(d) Contour of NO concentration in canyon with TiO₂ coating road.







(f) Contour of NO₂ concentration in canyon with TiO₂ coating road.

Fig.5 Flow fields, contours of flow velocity and NO_x concentration in the observed street canyons.

251 Profiles of NO and NO₂ concentration at the leeward wall, windward wall and the breathing zone are shown in Fig.6. The breathing zone is defined as a height of y=1.5 252 m because it is about the nose height of the pedestrians. Concentrations at leeward and 253 254 windward wall can influence the health of people who live or work in the buildings on 255 either side of the street. It is obvious that the NOx concentration is lower in street 256 canyons with TiO₂ coating road in all observed profiles. The average NO and NO₂ concentration at the height of breathing zone decrease by 3.29% and 3.88%, 257 258 respectively, under the influence of PCO reactions. The average NO concentration near the windward wall and leeward wall decrease by 3.28% and 3.35%, respectively. The 259 average NO₂ concentration near the windward wall and leeward wall decrease by 3.84% 260 261 and 3.95%, respectively. Conclusions can thus be drawn that the PCO reactions with TiO₂ coating decrease the NO_X concentration inside street canyon. However, the 262 263 characteristics of pollutant profiles are similar for street canyons with and without TiO₂

coating road. NO and NO₂ concentrations at windward wall reach high level at 0.25H \leq y \leq 0.75H. Conversely, NO and NO₂ concentrations at leeward wall at 0.25H \leq y \leq 0.75H are at a low level, while reaching the peak value at about y=0.05H. NO and NO₂ concentrations at breathing zone have the peak value near leeward wall (x \leq -0.2W). That means pedestrians near the leeward side are exposed to more pollution than at the windward side. PCO reaction with TiO₂ coating can lead to 3-4% reduction of NO and NO₂ in this area.



(a) Profiles of NO concentration at leeward and windward wall along 0<y<H



(c) Profiles of NO concentration at the

breathing zone along 0<x<W



(b) Profiles of NO₂ concentration at leeward and windward wall along 0<y<H



(d) Profiles of NO₂ concentration at the

breathing zone along 0<x<W

Fig.6 Profiles of NO and NO2 concentration.

4.2 Effects of irradiance on PCO and NO_x profiles

272	Irradiance (E) is varied in the range of 10-40 $W \cdot m^{-2}$ when analysing the effects of
273	irradiance on the PCO and NO _x profiles in street canyon. The relative humidity (50%)
274	is kept constant. Fig.7 shows the profiles of NO and NO ₂ concentration in relation to
275	irradiance. At leeward wall, the peak value of NO_x concentration is at ~0.05H. The peak
276	value decreases from 9.11ppm to 8.7ppm for NO, and from 0.92ppm to 0.87ppm for
277	NO ₂ , when irradiance increase from 0 to $40 W \cdot m^{-2}$. The reductions of NO and NO ₂
278	concentration are 4.5% and 5.4%, respectively. There is a sharp decrease along
279	$0.05H \le y \le 0.25H$. The NO _x concentration near the roof of the leeward building has a
280	small spike, reaching about 6 and 0.6 ppm for NO and NO ₂ , respectively. At windward
281	wall, the concentration is in constant change and much lower than the leeward wall. In
282	the breathing zone, the peak value of NO concentration is at about x=0.1W and ranges
283	from 8.5~9 ppm with varied irradiance. The concentration falls rapidly along
284	$0.1W \le x \le 0.2W$. The reaction rates of NO and NO ₂ are monotonic functions of the
285	irradiance (E), i.e. the increase of irradiance accelerates the reaction. NO and NO_2
286	concentrations in street canyon decrease when the irradiance increase.



(a) Profiles of NO concentration at leeward and windward wall along

0 < y < H



(b) Profiles of NO₂ concentration at

leeward and windward wall along

0 < y < H



1.0 -No Surface Reaction E=10W/m² 0.9 E=20W/m² E=30W/m² 0.8 Concentration (ppm) E=40W/m² 0.7 0.6 0.5 0.4 0.3 0.5 1.0 0.0 X/W

(c) Profiles of NO concentration at the

breathing zone along 0<x<W

(d) Profiles of NO₂ concentration at the

breathing zone along 0<x<W

Fig.7 Profiles of NO and NO2 concentration in conditions with varied irradiance.

Fig.8 presents the NO and NO₂ conversions. For both NO and NO₂, the conversion increases when the irradiance increases. The conversion at leeward wall, windward wall and breathing zone is similar. However, the average conversion of pollutants inside the whole street canyon is higher than all three zones. The PCO reaction happens on the ground while air flow still carries more pollutants to the ground and the buildings'

292 external surfaces. This explains why the NO_x is absorbed by the TiO₂ coating road but the lowest NO_x conversion is not at the breathing zone which is near the ground. 293 Average conversions of NO and NO₂ in street canyon reduce from 3.70% to 1.35% and 294 from 4.31% to 2.43%, respectively, when the irradiance decreases from 40 $W \cdot m^{-2}$ to 295 $10W \cdot m^{-2}$. It can be seen that the irradiance has a great effect on PCO reaction in a 296 297 street canyon with TiO₂ coating road. The higher the irradiance, the more effective the PCO reaction is. The NO₂ conversion is always higher than NO, which means NO₂ is 298 299 more sensitive to PCO reaction in the conditions set in this study.

300



(a) NO conversion (X_{NO}) as a function

(b) NO₂ conversion (X_{NO2}) as a function

of the irradiance.

of the irradiance.

Fig.8 Pollutant conversion as a function of the irradiance.

301 **4.3 Effects of relative humidity on PCO and NO_x profiles**

302 The effect of relative humidity on PCO and pollutant concentration in a street canyon

303 with TiO₂ coating road is studied by changing the relative humidity (RH) in the range

of 10-90%. The irradiance $(40 W \cdot m^{-2})$ is kept constant. Profiles of NO and NO₂ 304 305 concentration at leeward and windward are shown in Fig.9 (a) and (b). It can be seen that the characteristics of pollutant distribution along the walls are consistent with the 306 307 relative humidity. At leeward wall, the peak value of NO and NO₂ concentration is at x= \sim 0.05H, and the maximum rising rate is 2.5% (NO) and 1.7% (NO₂) when relative 308 309 humidity increases from 10% to 90%. NO and NO2 concentration at the windward side 310 increase more when the relative humidity increases, comparing with that at the leeward side, which see an increase of 5% (NO) and 3% (NO₂) when relative humidity increases 311 312 from 10% to 90%. NO and NO₂ concentration profiles at the breathing zone is shown 313 in Fig.9 (c)-(d). The NO and NO₂ concentration at the breathing zone rise from 2.6% to 5.3% and from 2.3% to 5.3%, respectively, when relative humidity increases from 314 315 10% to 90%. Lower relative humidity results in more effective PCO reaction and lower 316 NO_x concentration in street canyon.

317 Fig.10 shows the effect of relative humidity on NO_x conversion. It is clear that when 318 the relative humidity increases, the NO and NO₂ conversions decrease in street canyon. 319 The same tendency can be also seen from conversions at the leeward wall, windward 320 wall and breathing zone. However, the change rates in different locations are different. The average conversion of the whole street canyon is higher than the three zones when 321 322 relative humidity is 50%-90%. The gap between the average conversion of the whole 323 canyon and the zones gets narrower when the relative humidity decreases. When the relative humidity is 30%, the conversions of the four computational domains (whole 324

325 street cannon, leeward wall, windward wall and breathing zone) are similar. Average conversion of NO and NO₂ in street canyon decrease from 5.11% to 2.54% and from 326 5.60% to 3.25%, respectively, when the relative humidity increase from 10% to 90%. 327 328 Within the pollutant accumulated zone, NO and NO₂ conversion at leeward wall have the greatest change with the same change of relative humidity. Along the leeward wall, 329 330 the highest NO and NO₂ conversions are 5.77% and 5.23%, respectively, when RH=10%, and the lowest NO and NO₂ conversions are 1.17% and 1.71%, respectively, 331 332 when *RH*=90%.



(a) Profiles of NO concentration at leeward and windward wall along





(b) Profiles of NO_2 concentration at

leeward and windward wall along

0<y<H



0<y<H

(c) Profiles of NO concentration at the

(d) Profiles of NO₂ concentration at the

breathing zone along 0<x<W

breathing zone along 0<x<W

Fig.9 Profiles of NO and NO2 concentration in conditions with varied relative





(a) NO conversion (X_{NO}) as a function (b) NO₂ conversion (X_{NO2}) as a function of the relative humidity.

Fig.10 Pollutant conversion as a function of the relative humidity.

5. Conclusions and recommendations

A CFD model coupled with PCO reaction is implemented and validated with experimental data available in the literature for NOx abatement in a real urban street canyon with aspect ratio H/W=1. Irradiance and relative humidity are investigated, as the factors that can influence the behavior of the TiO₂ coating road with a representative TiO₂ concrete characteristic . Results show that TiO₂ coating road can effectively reduce NO_x concentration in the street canyon. The irradiance and the relative humidity have great effect on PCO reaction and on reducing the NO_x concentration in street canyon 341 with TiO_2 coating road. The higher the irradiance, the more effective the PCO reaction 342 is. When the relative humidity is increased, the NO and NO₂ conversions tend to 343 decrease.

344 CFD model implemented in this study can be readily used for the investigation of PCO reaction in street canyon with TiO₂ coating road. Different influencing factors can 345 346 be investigated using the model, allowing for fast and effective preliminary evaluation of several scenarios aiming at the photocatalytic process. According to experiment 347 studies (Faraldos et al., 2016; Fresno et al., 2014; Lasek et al., 2013), the behavior of 348 349 TiO₂ concrete is related to the type of TiO₂ concrete and the concentration of TiO₂. For 350 further studies, different types of TiO₂ concrete can be tested and evaluated. Other applications of TiO₂ coating may also be modeled and evaluated, for example, TiO₂ 351 352 paint coated on building facades.

353

354 ACKNOWLEDGEMENTS

355 The work described in this paper was financially supported by National Natural356 Science Foundation of China (No.50808124).

357

358 **References**

359 Ai, Z.T., Mak, C.M., 2017. CFD simulation of flow in a long street canyon under a

- 360 perpendicular wind direction: Evaluation of three computational settings.
- 361 Building and Environment 114, 293–306.
- 362 https://doi.org/10.1016/j.buildenv.2016.12.032
- 363 Allegrini, J., Dorer, V., Carmeliet, J., 2014. Buoyant flows in street canyons:
- 364 Validation of CFD simulations with wind tunnel measurements. Building and
- 365 Environment 72, 63–74. https://doi.org/10.1016/j.buildenv.2013.10.021
- 366 Allen, G., Janes, P., Nicholson, J., Dalton, J., Jones, N., Hallam, K., 2003.
- 367 Photocatalytic oxidation of NO x gases using TiO 2 : a surface spectroscopic
- 368 approach. Environmental Pollution 120, 415–422. https://doi.org/10.1016/s0269-
- 369 7491(02)00107-0
- 370 Alpert, S.M., Knappe, D.R.U., Ducoste, J.J., Blvd, P.P., 2010. Modeling the UV /
- 371 hydrogen peroxide advanced oxidation process using computational fluid
- dynamics. Water Research 44, 1797–1808.
- 373 https://doi.org/10.1016/j.watres.2009.12.003
- Baik, J.J., Kang, Y.S., Kim, J.J., 2007. Modeling reactive pollutant dispersion in an
- 375 urban street canyon. Atmospheric Environment 41, 934–949.
- 376 https://doi.org/10.1016/j.atmosenv.2006.09.018
- 377 Baker, J., Walker, H.L., Cai, X., 2004. A study of the dispersion and transport of
- 378 reactive pollutants in and above street canyons A large eddy simulation.
- 379 Atmospheric Environment 38, 6883–6892.
- 380 https://doi.org/10.1016/j.atmosenv.2004.08.051

- 381 Ballari, Hunger, Hüsken, HBrouwers, 2010. NOx photocatalytic degradation
- 382 employing concrete pavement containing titanium dioxide. Applied Catalysis B:
- 383 Environmental 95, 245–254. https://doi.org/10.1016/j.apcatb.2010.01.002
- 384 Ballari, M.M., Hunger, M., Hüsken, G., Brouwers, H.J.H., 2010. Modelling and
- 385 experimental study of the NO x photocatalytic degradation employing concrete
- 386 pavement with titanium dioxide 151, 71–76.
- 387 https://doi.org/10.1016/j.cattod.2010.03.042
- 388 Carpenter, L.J., Clemitshaw, K.C., Burgess, R.A., Penkett, S.A., Cape, J.N.,
- 389 McFadyen, G.G., 1998. Investigation and evaluation of the NO(x)/O 3
- 390 photochemical steady state. Atmospheric Environment 32, 3353–3365.
- 391 https://doi.org/10.1016/S1352-2310(97)00416-0
- 392 Chen, M., Chu, J.W., 2011. NOxphotocatalytic degradation on active concrete road
- 393 surface From experiment to real-scale application. Journal of Cleaner
- 394 Production 19, 1266–1272. https://doi.org/10.1016/j.jclepro.2011.03.001
- de Melo, J.V.S., Trichês, G., 2012. Evaluation of the influence of environmental
- 396 conditions on the efficiency of photocatalytic coatings in the degradation of
- 397 nitrogen oxides (NOx). Building and Environment 49, 117–123.
- 398 https://doi.org/10.1016/j.buildenv.2011.09.016
- 399 De Melo, J.V.S., Trichês, G., Gleize, P.J.P., Villena, J., 2012. Development and
- 400 evaluation of the efficiency of photocatalytic pavement blocks in the laboratory
- 401 and after one year in the field. Construction and Building Materials 37, 310–319.

402 https://doi.org/10.1016/j.conbuildmat.2012.07.073

- 403 Devahasdin, S., Fan, C., Li, K., Chen, D.H., 2003. TiO2photocatalytic oxidation of
- 404 nitric oxide: Transient behavior and reaction kinetics. Journal of Photochemistry
- 405 and Photobiology A: Chemistry 156, 161–170. https://doi.org/10.1016/S1010-
- 406 6030(03)00005-4
- 407 Diamanti, M. V., Del Curto, B., Ormellese, M., Pedeferri, M.P., 2013. Photocatalytic
- 408 and self-cleaning activity of colored mortars containing TiO2. Construction and
- 409 Building Materials 46, 167–174.
- 410 https://doi.org/10.1016/j.conbuildmat.2013.04.038
- 411 Einaga, H., Tokura, J., Teraoka, Y., Ito, K., 2015. Kinetic analysis of TiO 2 -catalyzed
- 412 heterogeneous photocatalytic oxidation of ethylene using computational fluid
- 413 dynamics. CHEMICAL ENGINEERING JOURNAL 263, 325–335.
- 414 https://doi.org/10.1016/j.cej.2014.11.017
- 415 Fan, W., Chan, K.Y., Zhang, C., Zhang, K., Ning, Z., Leung, M.K.H., 2018. Solar
- 416 photocatalytic asphalt for removal of vehicular NOx: A feasibility study. Applied
- 417 Energy 225, 535–541. https://doi.org/10.1016/j.apenergy.2018.04.134
- 418 Faraldos, M., Kropp, R., Anderson, M.A., Sobolev, K., 2016. Photocatalytic
- 419 hydrophobic concrete coatings to combat air pollution. Catalysis Today 259,
- 420 228–236. https://doi.org/10.1016/j.cattod.2015.07.025
- 421 Fluent, A., 2009. 12.0 Theory Guide. Ansys Inc 5.
- 422 Folli, A., Strøm, M., Madsen, T.P., Henriksen, T., Lang, J., Emenius, J., Klevebrant,

- 423 T., Nilsson, Å., 2015. Field study of air purifying paving elements containing
- 424 TiO2. Atmospheric Environment 107, 44–51.
- 425 https://doi.org/10.1016/j.atmosenv.2015.02.025
- 426 Fresno, F., Portela, R., Suárez, S., Coronado, J.M., 2014. Photocatalytic materials:
- 427 Recent achievements and near future trends. Journal of Materials Chemistry A 2,
- 428 2863–2884. https://doi.org/10.1039/c3ta13793g
- 429 García-yee, J.S., Torres-jardón, R., Barrera-huertas, H., Castro, T., Peralta, O., García,
- 430 M., 2018. Characterization of NO x -O x relationships during daytime
- 431 interchange of air masses over a mountain pass in the Mexico City megalopolis.
- 432 Atmospheric Environment 177, 100–110.
- 433 https://doi.org/10.1016/j.atmosenv.2017.11.017
- 434 Guo, M.Z., Ling, T.C., Poon, C.S., 2017. Photocatalytic NOx degradation of concrete
- 435 surface layers intermixed and spray-coated with nano-TiO2: Influence of
- 436 experimental factors. Cement and Concrete Composites 83, 279–289.
- 437 https://doi.org/10.1016/j.cemconcomp.2017.07.022
- 438 Han, B.S., Baik, J.J., Kwak, K.H., Park, S.B., 2018. Large-eddy simulation of reactive
- 439 pollutant exchange at the top of a street canyon. Atmospheric Environment 187,
- 440 381–389. https://doi.org/10.1016/j.atmosenv.2018.06.012
- 441 Hang, J., Luo, Z., Wang, X., He, L., Wang, B., Zhu, W., 2017. The influence of street
- 442 layouts and viaduct settings on daily carbon monoxide exposure and intake
- fraction in idealized urban canyons. Environmental Pollution 220, 72–86.

444 https://doi.org/10.1016/j.envpol.2016.09.024

- 445 Hao, C., Xie, X., Huang, Y., Huang, Z., 2019. Study on Influence of viaduct and noise
- barriers on the particulate matter dispersion in street canyons by CFD Modeling.
- 447 Atmospheric Pollution Research. https://doi.org/10.1016/j.apr.2019.07.003
- 448 Jelle Roegiers, 2018. CFD- and radiation field modeling of a gas phase photocatalytic
- 449 multi-tube reactor. Chemical Engineering Journal 287–299.
- 450 Jiang, Q., Qi, T., Yang, T., Liu, Y., 2019. Ceramic tiles for photocatalytic removal of
- 451 NO in indoor and outdoor air under visible light. Building and Environment 158,
- 452 94–103. https://doi.org/10.1016/j.buildenv.2019.05.014
- 453 Kikumoto, H., Ooka, R., 2012. A study on air pollutant dispersion with bimolecular
- 454 reactions in urban street canyons using large-eddy simulations. Journal of Wind
- 455 Engineering and Industrial Aerodynamics 104–106, 516–522.
- 456 https://doi.org/10.1016/j.jweia.2012.03.001
- 457 Kwak, K.H., Baik, J.J., Lee, K.Y., 2013. Dispersion and photochemical evolution of
- 458 reactive pollutants in street canyons. Atmospheric Environment 70, 98–107.
- 459 https://doi.org/10.1016/j.atmosenv.2013.01.010
- 460 Lasek, J., Yu, Y.H., Wu, J.C.S., 2013. Removal of NOxby photocatalytic processes.
- 461 Journal of Photochemistry and Photobiology C: Photochemistry Reviews 14, 29–
- 462 52. https://doi.org/10.1016/j.jphotochemrev.2012.08.002
- 463 Lira, J.D.O.B., Padoin, N., Vilar, V.J.P., Soares, C., 2018. Photocatalytic NO x
- 464 abatement : Mathematical modeling , CFD validation and reactor analysis.

- 465 Journal of Hazardous Materials 0–1.
- 466 https://doi.org/10.1016/j.jhazmat.2018.07.009
- 467 Macphee, D.E., Folli, A., 2016. Photocatalytic concretes The interface between
- 468 photocatalysis and cement chemistry. Cement and Concrete Research 85, 48–54.
- 469 https://doi.org/10.1016/j.cemconres.2016.03.007
- 470 Mendoza, J.A., Lee, D.H., Kang, J.H., 2017. Photocatalytic removal of gaseous
- 471 nitrogen oxides using WO3/TiO2 particles under visible light irradiation: Effect
- 472 of surface modification. Chemosphere 182, 539–546.
- 473 https://doi.org/10.1016/j.chemosphere.2017.05.069
- 474 Mills, A., Hunte, S. Le, 1997. An overview of semiconductor photocatalysis. Journal
- 475 of Photochemistry and Photobiology A: Chemistry 108, 1–35.
- 476 https://doi.org/10.1126/science.12.296.346-a
- 477 Moradpour, M., Afshin, H., Farhanieh, B., 2017. A numerical investigation of
- 478 reactive air pollutant dispersion in urban street canyons with tree planting.
- 479 Atmospheric Pollution Research 8, 253–266.
- 480 https://doi.org/10.1016/j.apr.2016.09.002
- 481 Mothes, F., Ifang, S., Gallus, M., Golly, B., Boréave, A., Kurtenbach, R., Kleffmann,
- 482 J., George, C., Herrmann, H., 2018. Bed flow photoreactor experiments to assess
- 483 the photocatalytic nitrogen oxides abatement under simulated atmospheric
- 484 conditions. Applied Catalysis B: Environmental 231, 161–172.
- 485 https://doi.org/10.1016/j.apcatb.2018.03.010

486	Muilwijk, C., Schrijvers, P.J.C., Wuerz, S., Kenjereš, S., 2016. Simulations of
487	photochemical smog formation in complex urban areas. Atmospheric
488	Environment 147, 470-484. https://doi.org/10.1016/j.atmosenv.2016.10.022
489	Muñoz, V., Casado, C., Suárez, S., Sánchez, B., Marugán, J., 2019. Photocatalytic
490	NOx removal: Rigorous kinetic modelling and ISO standard reactor simulation.
491	Catalysis Today 326, 82–93. https://doi.org/10.1016/j.cattod.2018.09.001
492	National Bureau of Statistics of China, 2019. China Statistical Yearbook, National
493	Bureau of Statistics of China.
494	National Ministry of Ecology and Environment of China, 2018. China Vehicle
495	Environmental Management Annual Report.
496	Notario, A., Bravo, I., Adame, J.A., Díaz-de-Mera, Y., Aranda, A., Rodríguez, A.,
497	Rodríguez, D., 2012. Analysis of NO, NO 2, NO x, O 3 and oxidant (OX=O
498	3+NO 2) levels measured in a metropolitan area in the southwest of Iberian
499	Peninsula. Atmospheric Research 104–105, 217–226.
500	https://doi.org/10.1016/j.atmosres.2011.10.008
501	Passalía, C., Alfano, O.M., Brandi, R.J., 2011. Modeling and Experimental
502	Verification of a Corrugated Plate Photocatalytic Reactor Using Computational
503	Fluid Dynamics 9077–9086. https://doi.org/10.1021/ie200756t
504	Ryerson, T.B., Williams, E.J., Fehsenfeld, F.C., 2000. An efficient photolysis system
505	for fast-response NO2measurements. Journal of Geophysical Research
506	Atmospheres 105, 26447–26461. https://doi.org/10.1029/2000JD900389

- 507 Salvado, I., 2007. Two-Dimensional Modeling of a Flat-Plate Photocatalytic Reactor
- 508 for Oxidation of Indoor Air Pollutants 7489–7496.
- 509 https://doi.org/10.1021/ie070391r
- 510 Salvado, I., Hargreaves, D.M., 2007. Evaluation of the Intrinsic Photocatalytic
- 511 Oxidation Kinetics of Indoor Air Pollutants 41, 2028–2035.
- 512 https://doi.org/10.1021/es0615690
- 513 Seinfeld, J.H., 2007. Global Atmospheric Chemistry of Reactive Hydrocarbons.
- 514 Reactive Hydrocarbons in the Atmosphere 293–319.
- 515 https://doi.org/10.1016/b978-012346240-4/50009-6
- 516 Sini, J.F., Anquetin, S., Mestayer, P.G., 1996. Pollutant dispersion and thermal effects
- 517 in urban street canyons. Atmospheric Environment 30, 2659–2677.
- 518 https://doi.org/10.1016/1352-2310(95)00321-5
- 519 Tokode, O., Prabhu, R., Lawton, L.A., Robertson, P.K.J., 2017. Journal of
- 520 Environmental Chemical Engineering A photocatalytic impeller reactor for gas
- 521 phase heterogeneous photocatalysis. Journal of Environmental Chemical
- 522 Engineering 5, 3942–3948. https://doi.org/10.1016/j.jece.2017.07.068
- 523 Vezzoli, M., Farrell, T., Baker, A., Psaltis, S., Martens, W.N., Bell, J.M., 2013.
- 524 Optimal catalyst thickness in titanium dioxide fixed film reactors : Mathematical
- 525 modelling and experimental validation. Chemical Engineering Journal 234, 57–
- 526 65. https://doi.org/10.1016/j.cej.2013.08.049
- 527 Xie, X., Zhu, Z., 2018. Effects of Heat Intensity and Inflow Wind on the Reactive

528	Pollution Dispersion in Urban Street Canyon. Journal of Shanghai Jiaotong
529	University (Science) 23, 109–116. https://doi.org/10.1007/s12204-018-2030-x
530	Yang, L., Hakki, A., Zheng, L., Jones, M.R., Wang, F., Macphee, D.E., 2019.
531	Photocatalytic concrete for NOx abatement: Supported TiO2 efficiencies and
532	impacts. Cement and Concrete Research 116, 57-64.
533	https://doi.org/10.1016/j.cemconres.2018.11.002
534	Yu, Q.L., Ballari, M.M., Brouwers, H.J.H., 2010. Indoor air purification using
535	heterogeneous photocatalytic oxidation. Part II: Kinetic study. Applied Catalysis
536	B: Environmental 99, 58-65. https://doi.org/10.1016/j.apcatb.2010.05.032
537	Zhang, W., 2014. Experimental studies on automobile exhaust photocatalytic
538	degradationly Asphalt pavement Material. Chang'an University.
539	Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi,
540	J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., Zhang, Q., 2018. Trends in
541	China's anthropogenic emissions since 2010 as the consequence of clean air
542	actions. Atmospheric Chemistry and Physics 18, 14095–14111.
543	https://doi.org/10.5194/acp-18-14095-2018