Study of nitric oxide degradation properties of photoactive concrete containing nitrogen and/or carbon co-modified titanium dioxide – preliminary findings

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In recent years, titanium dioxide (TiO_2) has been commonly applied in the production of photoactive concrete materials capable of degrading a wide range of air contaminant such as nitric oxide (NO), VOC etc. It was confirmed that the photocatalytic activity of TiO_2 can be further enhanced by modifying the photocatalyst with non-metals such as nitrogen (N) or carbon (C). In view of this finding, several concrete/TiO_2 composites consisting of commercial concrete and raw anatase TiO_2 (supplied by Grupa Azoty Zakłady Chemiczne 'POLICE' S.A., Poland), previously modified with ammonia [N source] and/or 2-propanol [C source] have been manufactured. For reference, the additional concrete samples were prepared, containing unmodified TiO_2 and commercial titania P25 (Evonik). The NO degradation properties of prepared photoactive concrete materials were evaluated using laboratory test set-up. The measurements were conducted under constant temperature and humidity conditions, using ultraviolet light irradiation. Significant NO removal was recorded for the TiO_2/concrete composites containing N and/or C co-modified titania. The results were related to the improved photocatalytic activity of modified photocatalysts and probable, partial NO reduction to N_2, via the selective catalytic reduction process catalysed by TiO_2.
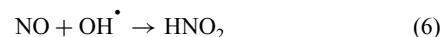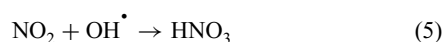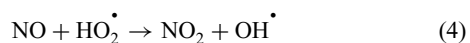
1. Introduction: Air pollution poses a grave threat to human health and environment. Especially, a complex mix of hazardous compounds has become an increasing share of emission in urban areas as a result of industrial activities, heating systems and road traffic. It should be emphasised that nitrogen oxides (NO_x) gases as the major air pollutants participate in the formation of photochemical smog and ozone [1].

Addressing air quality issues, the new alternative methods of purifying air such as heterogeneous photocatalysis are intensively studied. Utilisation of ultraviolet (UV) irradiation and semiconductor particles presence, mainly titanium dioxide (TiO_2), allow to completely decomposing of variety contaminants [2]. In particular, the extension of light absorption spectrum [3] and the high electron–hole separation efficiency are favourable for the expanded photocatalytic properties of TiO_2 [4], what has been merely achieved by various types of modification of the photocatalyst structure with non-metals or metals ions [5]. Among these efforts, doping with nitrogen (N) as well as carbon (C) has been merely found as an effective and feasible approach to improve TiO_2 properties [6–8].

The general mechanism of the photocatalytic NO_x oxidation was presented below. Hydrogen and hydroxide ions are dissociated from water. The active oxygen species are produced on the TiO_2 surface

$$O_2 + e^- \rightarrow O_2^- \tag{1}$$

$$OH^- + h^+ \rightarrow OH^\bullet \tag{2}$$

$$H^+ + O_2^- \rightarrow HO_2^\bullet \tag{3}$$

The reactivity of the generated oxygen species leads to the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) which, in turn, produces nitric acid or nitrous acid

$$NO + HO_2^\bullet \rightarrow NO_2 + OH^\bullet \tag{4}$$

$$NO_2 + OH^\bullet \rightarrow HNO_3 \tag{5}$$

$$NO + OH^\bullet \rightarrow HNO_2 \tag{6}$$

Basically, the degradation of NO_xs by photocatalysis can be described as follows:

$$NO \rightarrow HNO_2 \rightarrow NO_2 \rightarrow HNO_3 \tag{7}$$
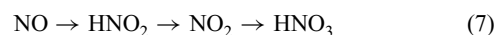
The reaction products as water soluble nitrate compounds could be flushed from the active surface of building materials by rain. As Matsuda *et al*. [9] accentuated the nitrate compounds can be subsequently extracted from the rain by a standard sewage plant. On the contrary, the incomplete NO oxidation may lead to the formation of the more toxic NO_2 gas [10].

NO_x air emissions can be reduced by selecting appropriate materials. In the development of the new photoactive construction materials, the self-cleaning property of TiO_2 makes it an ideal additive to building surfaces as paving surface or building facades [11–14]. Folli *et al*. [15] in a study tested the photocatalytic paving blocks with TiO_2-based layer, the conversion of NO reached values as high as 78% with low amount of NO_2 formed. Hüsken *et al*. [16] investigated efficient degradation of NO using concrete paving blocks containing photocatalytic active TiO_2. It was proved that the humidity of the process as well as the structure surface of active area impacting significance on NO degradation. Furthermore, an important relationship was established between the TiO_2 content in construction material and the photocatalytic process. Lucas *et al*. [17] revealed that even low addition of nanoparticles as 0.5 and 1 wt.% to building material impacted on high NO_x degradation rates. However, excessive content of catalyst on the mortar surface caused the decrease in photocatalytic activity of mortar composites.

In this Letter, we present preliminary results reporting on NO degradation properties of composite materials consisting of commercial concrete and N and/or C co-modified TiO_2 photocatalysts.

Table 1 Chemical compositions (%) of the commercial concrete and raw TiO_2

|	Concrete	TiO_2
SiO_2	19.4	—
Al_2O_3	3.3	—
Fe_2O_3	2.9	—
CaO	61.6	—
MgO	3.0	—
Na_2O	0.2	—
K_2O	0.5	—
TiO_2	—	99.7

2. Experimental results

2.1. Materials and methods: Commercial concrete (Betonfix, Kreisel Sp. z o.o., Poland) and raw TiO_2 (supplied by Grupa Azoty Zakłady Chemiczne 'POLICE' S.A., Poland) were used as a base materials for the preparation of photoactive concretes. The chemical compositions of the cement and TiO_2 are listed in Table 1. Synthetic gaseous ammonia (Messer, Poland) and 2-propanol (Avantor Performance Materials Poland S.A.) were used as N and C sources, respectively. All reagents were used as received without further purification.

Concrete samples for NO oxidation tests were prepared according to the procedure described in detail in our previous work [18]. In brief, the preparation method consisted of several steps: (i) modification of the TiO_2 with gaseous ammonia (N source) and/or 2-propanol (C source) at 300°C, (ii) mechanical grinding of the obtained N and/or C-modified TiO_2 photocatalysts with commercial concrete (at a 10:90 weight ratio), (iii) blending of the concrete/TiO_2 homogenous mixtures with water [water-to-concrete ratio (w/c) = 0.48] and (iv) casting the prepared slurries into cubical moulds (20 × 20 × 6 mm), and curing the samples for 28 days in ambient temperature. The as-prepared concrete materials were labelled as Con + TiO_2/N, Con + TiO_2/C and Con + TiO_2/N, C. For reference, the additional concrete samples were prepared, containing 10 wt.% of unmodified TiO_2 (Con + unTiO_2) or commercial photocatalyst P25 (Con + P25), manufactured by Evonik (Germany). In case of the concrete loaded with P25 photocatalyst, the w/c was changed to 0.80 due to the significant increase of concrete paste density caused by addition of P25. This allowed avoiding too rapid setting time of the prepared material.

The phase compositions of the materials were determined by utilising the Philips X'Pert X-ray diffractometer, equipped with a Cu X-ray source (λ Kα = 1.54 Å). The C and N contents in the TiO_2 photocatalysts, added to the concrete samples were determined using multi-N/C C analyser equipped with solids modules – high-temperature combustion system HT 1300 (Analytic Jena, Germany) and ONH 836 elemental analyser (Leco Corporation, USA). The surface properties of the photocatalytic additives were examined by applying the Fourier transform infrared spectroscopy (FTIR) 4200 spectrophotometer (Jasco, Japan), equipped with a diffuse reflectance accessory (Harrick, USA).

2.2. Photocatalytic NO oxidation: The photocatalytic activity of the prepared concrete samples was evaluated by removal of the NO gas from air stream. The NO degradation tests were conducted using the experimental set-up (Fig. 1) composed of: S – NO/air gas supply source, M – mass flow meter, R – photocatalytic reactor and A – chemiluminescence NO/NO_2 analyser (Model T200, Teledyne Advanced Pollution Instrumentation, USA).

The photocatalytic reactor consisted of cylindrical Pyrex glass chamber (with a total volume of 0.5 dm^3) and four UV–visible (vis) lamps (Actinic BL TL-E 22W, Philips), with the cumulative radiation intensity of 60 W/m^2 UV and 20 W/m^2 vis. The
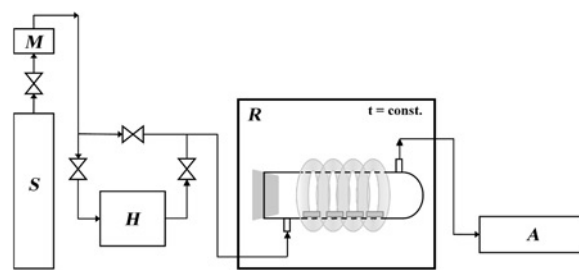
Fig. 1 *Experimental set-up used in the photocatalytic NO oxidation tests*

measurements were carried out at an NO inlet concentration of 1 ppm in air, under constant temperature (25°C) and continuous gas flow of 200 cm^3/min. The humidity level of the NO flow was set at 50% by passing gas stream through a humidification chamber (H, Fig. 1). All the photocatalytic oxidation experiments were performed according to the following procedure. Four concrete samples were placed in a central part of the reactor. After assembling the samples, the reactor was tightly closed and the NO gas stream was introduced under dark conditions for 30 min. When the concentration of the NO reached equilibrium (~1 ppm), the lamps were switched on and the concentration changes of the NO, NO_2 and NO_x (defined as the sum of NO and NO_2) were continuously measured for a further 30 min.

Due to the fact that the NO_2 gas is more toxic than NO, the effectiveness of concrete samples in NO removal ought to be estimated by the NO (φ_{NO}) or NO_x (φ_{NOx}) conversion in conjunction with the NO_2 selectivity (γ_{NO2})

$$\varphi_{NO} = \frac{[NO]_{in} - [NO]_{meas}}{[NO]_{in}} \times 100\% \tag{8}$$

$$\gamma_{NO_2} = \frac{[NO_2]_{meas}}{[NO]_{in} - [NO]_{meas}} \times 100\% \tag{9}$$

$$\varphi_{NO_x} = \frac{[NO_x]_{in} - [NO_x]_{meas}}{[NO_x]_{in}} \times 100\% \tag{10}$$

3. Results and discussion: The X-ray powder diffraction patterns of commercial concrete and exemplary TiO_2-containing concrete materials are shown in Fig. 2.
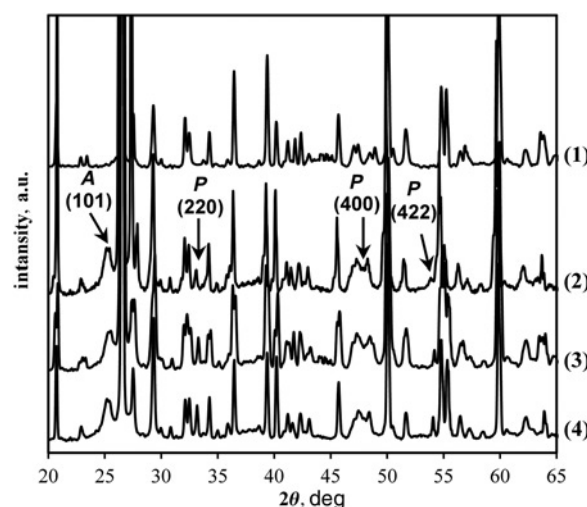
Fig. 2 *XRD patterns of (1) commercial concrete and obtained TiO_2/concrete composites: (2) Con + TiO_2/N, (3) Con + TiO_2/C and (4) Con + TiO_2/N,C*

The comparison of the X-ray diffraction (XRD) patterns of the TiO$_2$-loaded concretes with the JCPDS Card No. 21–1272 confirmed the presence of peaks (at $2\theta = 25.3°$ and $27.4°$) characteristic for the anatase (A) phases TiO$_2$. Moreover, the XRD results of the Con + TiO$_2$/N,C sample revealed the presence of additional reflections (at $2\theta = 33.0°$, $47.5°$ and $54.1°$), which were not observable in the TiO$_2$-free concrete sample. The described peaks were also present in the XRD patterns of the remaining TiO$_2$/concrete samples (Con + TiO$_2$/N and Con + TiO$_2$/C), and were ascribed to the perovskite-type oxide – calcium titanate (CaTiO$_3$) (P). Owing to the presence of TiO$_2$ in concrete matrix, it was assumed that CaTiO$_3$ is a product of reaction between the titania and CaCO$_3$ (one of the components of concrete). It should be noted that this process is known to typically occur at high temperature exciding 1000°C. However, according to Manafi et al. [19] the prolong grinding of the CaCO$_3$ and TiO$_2$ mixture may result in the intensification of kinetic energy of the system. This leads to the temperature increases which provide the needed energy for the formation of new stable phase – CaTiO$_3$. The presence of CaTiO$_3$ in the TiO$_2$/concrete samples was considered as relevant finding because it was confirmed that perovskite-type oxides can exhibit promising activity for the reduction of NO$_x$ [20, 21]. However, in order to assess the possible impact of the CaTiO$_3$ presence on the NO degradation properties of the obtained TiO$_2$/concrete samples additional studies need to be conducted.

Fig. 3 shows the NO concentration against time plots recorded for the representative samples.

During the initial 30 min of the experiment, the measured NO concentration in the outlet gas stream was first close to ~0 ppm level and then gradually increased to its initial inlet value (~1 ppm). This effect was presumably caused by the non-contaminated air removal from the reactor as well as by the adsorption of NO on the surface of the samples. After the UV–vis irradiation was turned on, a significant decrease in the NO concentration was observed, indicating the ongoing conversion of NO via photocatalytic oxidation process. It should be noted that contrary to expectations, after the light source was turned off, the NO oxidation was spontaneously progressing for additional 5 min, before the original NO inlet concentration was reached. As a matter of principle, no conversion should take place after removing the light source. However, it is believed that the already formed hydroxyl radicals can sustain the oxidation process, until these substances are entirely consumed by NO molecules.

Fig. 4 displays the NO, NO$_x$ conversion and NO$_2$ selectivity evaluated for the respective concrete samples after 30 min of irradiation.

It should be pointed out that the sample of TiO$_2$-free concrete proved to be completely inactive during the photocatalytic NO oxidation process. In case of the prepared TiO$_2$/concrete composites
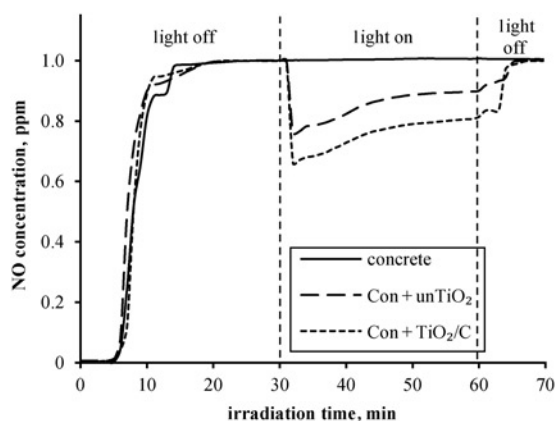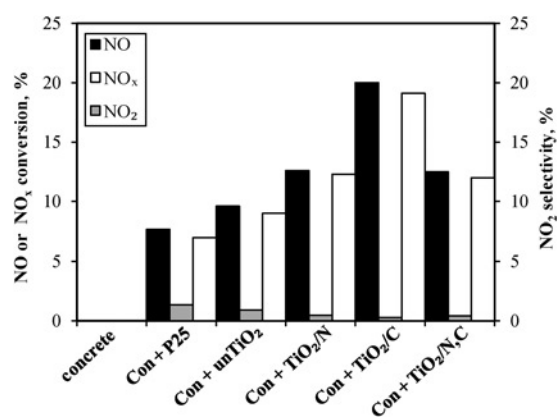

Fig. 4 NO, NO$_x$ conversion and NO$_2$ selectivity of the respective concrete samples measured after 30 min of irradiation

the NO conversion varied from ca. 8 to 20%, depending on the type of the photocatalytic additive. Moreover, it ought to be noted that the calculated NO and NO$_x$ conversion values for the individual TiO$_2$/concrete sample were closely similar. This effect was well reflected by the general law NO$_2$ selectivity of the materials, resulting in the limited generation of NO$_2$ molecules during the NO oxidation process. The reason for the reduced formation of the NO$_2$ is most likely related to the alkali character of the concrete matrix, capable of not only attracting the acidic NO to its surface, but also adsorbing the formed NO$_2$ molecules [22]. Soylu et al. [23] also stated that the produced NO$_2$ can be adsorbed on the surface of the TiO$_2$ photocatalyst in form of a chemisorbed NO$_2$, nitrites and nitrates, resulting in a further decrease of the NO$_2$ signal. As presented in Fig. 4, the NO conversion was notably lower for the referential concrete samples, Con + P25 and Con + unTiO$_2$, reaching ca. 8 and 9%, respectively. The higher NO conversion of the remaining concrete materials (in range of ca. 13–20%), containing N and/or C-modified TiO$_2$ additives, is believed to be connected with the presence of the non-metals in the TiO$_2$ structure. The higher photocatalytic activity of such modified photocatalysts was confirmed in the variety of photocatalytic oxidation processes [24–27] and ascribed to the formation of additional energy states in TiO$_2$ lattice. As presented in Table 2, the TiO$_2$/N and TiO$_2$/N,C photocatalysts displayed similar amounts of N, which might explain an almost identical NO (and NO$_x$) conversion on the Con + TiO$_2$/N and Con + TiO$_2$/N,C materials.

Moreover, in view of the FTIR results (Fig. 5) indicating the presence of NH$_4^+$ groups (at 1440 cm^{-1}) on the surface of the TiO$_2$/N and TiO$_2$/N,C additives, the higher effectiveness of the Con + TiO$_2$/N and Con + TiO$_2$/N,C concrete samples in NO removal could have been additionally caused by the partial NO reduction to N$_2$, with accordance to the selective catalytic reduction (SCR) mechanism, in with the TiO$_2$ acts as catalysts [28, 29]

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (11)$$
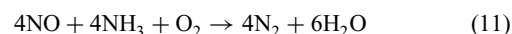
Furthermore, Komatsubara et al. [30] confirmed that in the presence of C-based species, the SCR process can be effectively conducted not only at room temperature [31], but also in the absence of

Fig. 3 NO concentration against irradiation time plots recorded for the representative concrete samples

Table 2 Content of the N and C elements in the modified TiO$_2$ added to the concrete

TiO$_2$ additive	Nitrogen content, wt.%	Carbon content, wt.%
TiO$_2$/N	0.27	—
TiO$_2$/C	—	1.38
TiO$_2$/N,C	0.32	0.26
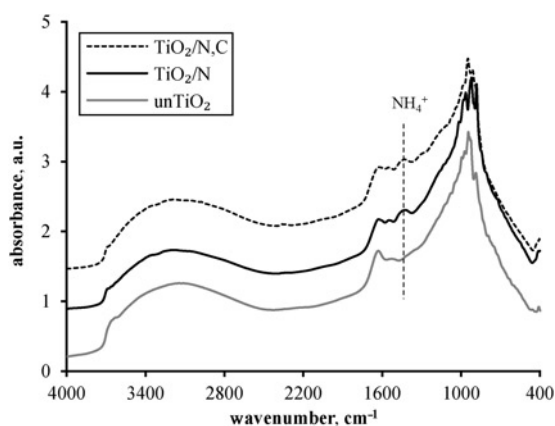
Fig. 5 *FTIR/DRS spectra of: N-modified, N,C-modified and unmodified TiO₂ photocatalysts present in concrete samples*

ammonia [32]. The presented literature findings might explain the higher NO removal effectiveness of the Con + TiO₂/C sample (Fig. 4), containing relatively high amount of C (Table 2) in its structure. However, detail explanation of this fact needs further studies.

4. Conclusions: Synopsizing the information presented in this Letter, the following conclusions can be drawn:

● The addition of N and/or C co-modified TiO₂ into commercial concrete allowed to obtain titania/concrete composite materials capable of effectively removing NO from air via photocatalytic oxidation process.

● In comparison to the TiO₂/concrete composites containing commercial P25 or unmodified TiO₂, the concrete materials loaded with N and/or C-modified photocatalysts exhibited notably higher NO oxidation properties. The superior NO removal effectiveness of the latter materials was ascribed to: (i) the increase of the photocatalytic activity of N and/or C-modified photocatalysts associated with the formation of additional energy states in TiO₂ lattice and (ii) probable, partial NO reduction to N₂, via the SCR process catalysed by TiO₂.

● The XRD analysis of prepared TiO₂/concrete composites revealed the presence of new phase – CaTiO₃, which is known to exhibit promising activity for the reduction of NOₓ. However, this issue requires further study.

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