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Review

A Review of Photocatalytic Materials for Urban NOx Remediation

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Abstract: NOx is a pervasive pollutant in urban environments. This review assesses the current state of the art of photocatalytic oxidation materials, designed for the abatement of nitrogen oxides (NOx) in the urban environment, and typically, but not exclusively based on titanium dioxide (TiO_2). Field trials with existing commercial materials, such as paints, asphalt and concrete, in a range of environments including street canyons, car parks, tunnels, highways and open streets, are considered in-depth. Lab studies containing the most recent developments in the photocatalytic materials are also summarised, as well as studies investigating the impact of physical parameters on their efficiency. It is concluded that this technology may be useful as a part of the measures used to lower urban air pollution levels, yielding ∼2% NOx removal in the immediate area around the surface, for optimised TiO_2, in some cases, but is not capable of the reported high NOx removal efficiencies >20% in outdoor urban environments, and can in some cases lower air quality by releasing hazardous by-products. However, research into new material is ongoing. The reason for the mixed results in the studies reviewed, and massive range of removal efficiencies reported (from negligible and up to >80%) is mainly the large range of testing practices used. Before deployment in individual environments site-specific testing should be performed, and new standards for lab and field testing should be developed. The longevity of the materials and their potential for producing hazardous by-products should also be considered.

Keywords: photocatalysis; NOx; titanium dioxide; NO abatement; concrete; air purification

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1. Introduction

Semiconductors, in particular titanium dioxide (TiO_2), have been used for photocatalytic oxidation (PCO) in a number of fields since at least the 1980s [1]. These include self-cleaning or 'easy-cleaning' outdoor surfaces, pollutant remediation from water, and abatement of volatile organic compounds (VOCs) in indoor air, with varying degrees of success [2–4]. This review will focus on their use when incorporated into outdoor surfaces for the remediation of urban nitrogen oxides (NOx), as a passive system utilising sunlight for activation and wind for mixing. There is a great deal of interest in this use as a fast, easy and inexpensive solution to the issue of high levels of NOx present in the urban environment. Its efficacy in these environments is still unproven however.

1.1. The Issue of Urban NOx Pollution

NOx, and in particular NO_2, is a burning issue in the urban environment. It is typically formed and released during high temperature combustion, for instance in engines, where the presence of nitrogen and oxygen in the inlet air form NOx [5]. This means it is particularly an issue in congested urban environments where it can regularly exceed threshold limits set by the European Union and World Health Organisation [5–8]. As NOx is produced in situ along roadways in urban environments, it is a good candidate for abatement by photocatalytic (PC) surfaces in the urban environment.

NO_2 is both a hazardous pollutant itself, associated with a range of chronic and acute health impacts [5], and is a part of the smog-ozone cycle, meaning its emissions contribute directly and indirectly to worsening local air quality [9,10]. The release of reactive nitrogen into the atmosphere also initiates a cascade of chemical processes that negatively impact human and ecosystem health more broadly [11]. Therefore, there are both scientific and political drivers for action to reduce NOx in urban environments, the European Directive 1999/30/EC dictates a maximum NO_2 concentration in ambient air of 40 $\mu g\ m^{-3}$ (21 ppb) averaged yearly and 200 $\mu g\ m^{-3}$ (104 ppb) hourly, which is not to be exceeded more than 18 times per year [6]. This means that, for compliance with the directive, NO_2 abatement methods must be evaluated over the complete diurnal and seasonal variations present each year. For instance, high performance during day time in the summer months may be balanced against poorer performance in dark, wet winter months, and zero removal during night time.

1.2. Possible NOx Removal Methods

One of the potential technologies for NOx abatement is photocatalytic (PC) surfaces. These surfaces can take many forms, but are most commonly concrete or asphalt, either pre-cast with TiO_2 or sprayed with a TiO_2 emulsion, otherwise paints that contain TiO_2 and can be sprayed onto walls, tunnels, sound barriers and other smooth vertical surfaces.

There are currently a number of commercial products available which claim to perform this function, as well as many recent laboratory studies into its improvement, these are described in the results Section 2. Photocatalytic oxidation (PCO) for NOx removal is an attractive proposition for local governments, as well as private businesses, due to its ease of use, instant impact and low cost when compared with other methods for ambient NOx removal [12]. However, the available field studies show very mixed results in terms of real-world performance, with reported removal efficiencies (REs) ranging from <2–80%.

Other solutions for lowering NOx involve source reduction through exhaust treatments, as well as behavioral changes, which include increasing the use of public transport or 'active' transport (e.g., cycling), relative to car use [13]. These methods may be effective in lowering ambient NOx levels until long-term solutions can be realised via zero-emission vehicles, for instance, hydrogen fuel cell or battery powered. However, these may be less attractive to bodies aiming to lower urban NOx due to their slower impact and/or high upfront cost [14]. On the other hand, other pollutants besides NOx must also be considered. In the UK for instance, a comparison of NOx abatement strategies found that retrofitting busses and replacing older diesel cars would be more cost-effective per ton of NOx than PC coatings, particularly when the co-benefits of increased fuel-efficiency and lower emissions of other species were considered [14].

There are still many questions remaining over the use of PC surfaces, both ideological questions over whether it is better to reduce the source emissions of NOx and associated emissions from combustion, rather than attempting to remove only dilute NOx from ambient air, but also practical questions. These include concerns over the production of harmful byproducts, conversion of NO to NO_2 without removal, longevity under real-world conditions, release of TiO_2 nanoparticles, and whether enough air can physically interact with the surface under representative conditions to provide significant removal. The magnitude of potential benefits must be weighed against costs, relative to other technologies, for individual scenarios. This review will focus on the efficacy of PC surfaces for NOx removal in real-world environments and whether they are a viable solution in principle, not the economic considerations.

1.3. Photocatalytic Surface Principle of Operation

The operating principle of TiO_2 photocatalytic surfaces is detailed in depth in a number of works [15–17] and so will only be briefly described here.

TiO_2 is a semiconductor with a band gap corresponding to wavelengths of light at ∼390 nm (3.2 eV) [16]. The stable polymorphs of TiO_2 that are active for PC are anatase and rutile TiO_2 [18,19], and typically a mix of these is used in PC products, such as the standard material P25 Evonik [20].

When a TiO_2 surface is exposed to UV radiation < 390 nm in wavelength, electrons (e^-) are excited from the valence to the conduction band, leaving a hole (h^+) in the conduction band and creating an e^-/h^+ pair (see Figure 1). There are different pathways possible after this point, including recombination of the e^-/h^+ pair, but the e^- also has enough potential energy to reduce O_2 into O_2^- superoxide radicals, and the h^+ sufficient energy to oxidise water and form OH, hydroxyl radicals. These reactive radical species can then initiate reaction cycles with a number of species, including NO [16,21]. Oxidation of NO to HNO_3, which results in removal from the atmosphere, occurs through reaction with OH and moves sequentially through to HNO_3 via HONO and NO_2, this is shown in Equations (1)–(5), reproduced from Patzsch et al. (2017) [21]. The solid HNO_3 that is produced at the surface will build-up until it is removed by dissolution in water, either from rainfall or manual washing, until that time HNO_3 build-up will lower the efficiency of the surface [21].

$$TiO_2 \xrightarrow{h\nu} e_{cb}{}^- + h_{vb}{}^+ \tag{1}$$

$$H_2O + h_{vb}{}^+ \longrightarrow H^+ + OH^\bullet \tag{2}$$

$$NO + OH^\bullet \longrightarrow HONO \tag{3}$$

$$HONO + OH^\bullet \longrightarrow NO_2 + H_2O \tag{4}$$

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

This sequential process is important as it means that when NO oxidation occurs slowly, for instance at high humidity (RH > 70%), gaseous NO_2 may be released before it is converted to HNO_3 [22]. According to more recent research conducted by Patzsch et al. (2017) [21], release of NO_2 may also be due to back-reduction of NO_3^- that has built up on the PC surface. Conversion of NO to the more toxic NO_2 would represent a negative net impact from the PC material. Other reactions pathways are also possible, including direct oxidation of NO to HNO_3 via reaction with HO_2 hydroperoxyl radicals [23], these pathways are summarised in a report made for the Environmental Industries Commission [12].

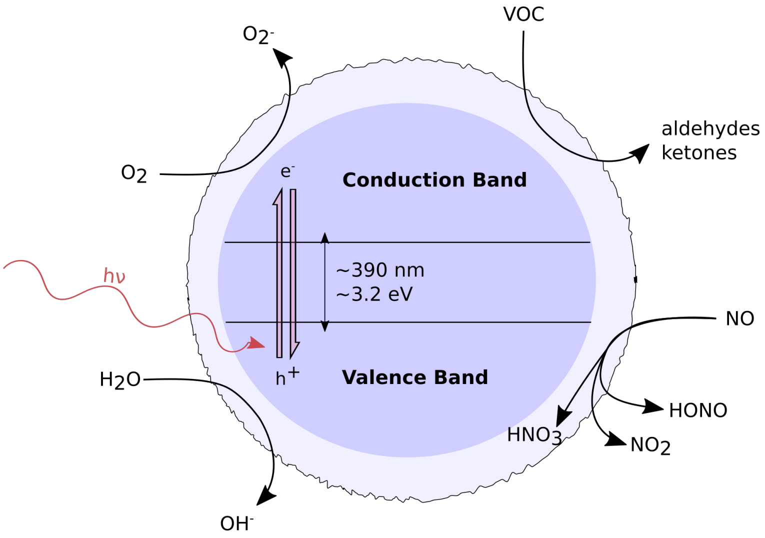

Figure 1. Excitation of TiO_2 and possible outcomes, VOC is Volatile Organic Compound.

There is potential for the formation of side products other than NO_2 as a result of NO oxidation in humid air, including HONO, H_2O_2, N_2O and O_3 [12,24]. These by-products are evidenced in a number of studies on pure TiO_2 [25–29] and are either detrimental to air quality directly, do not result in net reduction of NOx, and/or contribute to ozone production. The three recent reviews on this topic highlight the need for further analysis of by-product formation [24,30]. TiO_2 is not selective to reaction with NOx only, as described previously, reactive radical species are produced, that do not discriminate between NOx and other reactants. Depending on the co-pollutants present, other by-products can be formed, for instance VOC oxidation to aldehydes [31–34], this may also poison the PC surface and inhibit NOx oxidation. The oxidation of ammonia by PC surfaces, resulting in the release of gaseous HONO has also been observed [35]. This further complicates analysis of the impact of PC surfaces on overall air quality.

Knowledge of the PC operating principle can be used to develop improvements to the surfaces. The key areas for improvement are selectivity of NOx oxidation to HNO_3, activity under visible light and resistance to poisoning/improvements in durability. A large number of methods focusing either on the active material itself, or its support are currently undergoing development and are discussed in Section 2.1.3.

1.4. Previous Reviews

There has not been a peer-reviewed journal previously published on this exact topic, of PC materials for the abatement of ambient urban NOx, however, reports have been made for governmental bodies [12,24,30], and review articles on more specific aspects of NOx removal by PC methods have been published, such as: projects in Belgium only [36], indoor air [3], PC concrete in Belgium [37] and photocatalytic concrete [38,39]. Reviews on more general use of TiO_2 photocatalysis, including self-cleaning materials, indoor air cleaners and pollution remediation in water and waste streams, as well as the fundamentals of TiO_2 photocatalysis have also been published [1,2,15–17,40–48].

The two most relevant, review style, publications to this article are the report on 'Paints and Surfaces for the Removal of Nitrogen Oxides' prepared by the Air Quality Expert Group (AQEG) in 2016 [24] and the Environmental Industries Commission (EIC) report titled: 'Towards Purer Air: A review of the latest evidence of the effectiveness of photocatalytic materials and treatments in tackling local air pollution' (2017) [12]. They both present an overview of recent field studies, as well as briefer overviews of lab studies and modelling simulations and both end with their own model for PC NOx abatement.

The overall outlook of the AQEG report is negative and claims that the studies reporting considerable NOx reductions use unrealistic conditions. They go so far as to say that further study is not recommended, due to the lack of compelling field evidence, the poor results from their model, and the potential for production of unwanted by-products as a consequence of PC material deployment [24]. Conversely, the IEC report takes a more positive view of TiO_2 based PCO, quoting mixed results from the field studies but claiming that: 'substantial reductions in ambient NOx levels were observed' in some studies. They also produce their own model which reports much greater NOx reduction than the AQEG model. They believe further field trials should be conducted and make a series of recommendations for future trials [12]. The legitimacy of these stances will be investigated during this review.

1.5. Scope and Method

There is a general consensus that TiO_2 can photocatalytically oxidise NOx when excited by UV light under controlled lab conditions, although with varying efficiency depending on the material, its support, and the prevailing test conditions. Therefore, this review will summarise recent and pertinent lab studies, however the main focus of the review is evidence from field studies, pertaining to whether the surfaces can provide significant NOx removal under real-world conditions. In this area there is not a general consensus, studies that appear similar report a massive variety of REs, from a large number reporting negligible NOx abatement to studies reporting NOx removal of >80%, as well as other studies reporting an increase in NOx concentration after application of PC materials.

This review was conducted by first analysing all related articles from the Web of Science (WOS) database from 2017 onwards, using the following key words: photocatalytic surfaces, photocatalytic materials, ambient air NOx removal, TiO_2, SnO_2. After analysis of the articles, it was concluded that this did not contain a sufficient number of field studies, and the search was widened to include all articles from the WOS and Scopus databases from 2005 onwards that matched the key-words. The bibliographies of the chosen articles were then manually reviewed, and papers citing the key articles were also searched, to identify pertinent references. Initially, only peer-reviewed articles were considered but, due to the nature of this field, there are many academic-commercial partnerships and resulting technical reports, conference proceedings and theses, they contain some of the larger field studies, and are cited in other reviews, and were therefore also included for completeness.

2. Results

The literature on this subject can be roughly split into lab studies, which typically showcase new material improvements or demonstrate the impact of varying environmental parameters on the performance of existing materials, and field studies where the impact of PC deployments in urban environments is quantified. There are also a small number of modelling studies, which aim to translate the lab studies into performance in the field. Some studies contain both lab and field components and are included in the section that appeared most relevant, but may be referenced in other sections.

The lab studies are split into studies related to, the impact of physical parameters on removal, the durability of surfaces, and improvements to materials. The field studies are split into sections depending on whether the PC surface is on (1) streets, i.e., horizontal surfaces such as concrete or asphalt on roads and pavements, (2) walls, i.e., vertical surfaces, typically using PC paints, or (3) semi-enclosed environments such as tunnels and car parks.

2.1. Laboratory Results

When comparing laboratory studies, it is important to note the conditions that were used for obtaining the results as, particularly for removal efficiency (RE), a relative measure, the final results will depend on external parameters as well as the actual material tested. Approximately half of all the lab studies investigated use the ISO standard 22197-1:2007 [49] (now superseded by BS ISO 22197-1:2016 [50]) which contains a specific test method for determining the performance of PC materials when purifying nitric oxide (NO) from air. It stipulates values for NO concentration (1 ppm), airflow (3 L min^{-1}), irradiance (10 W m^{-2}) and sample area (49.5 mm ± 0.5 mm by 99.5 mm ± 0.5 mm), where these standards are followed this is noted, otherwise a description of the conditions is given. A smaller number of studies also use the similar Japanese Standards Association (JSA) standard JIS R 1701-1:2004 [51].

A different strategy for delivering results that transfer across studies is to compare materials to a commercially available standard material, such as Evonik Degussa P25, which is made up of 20 nm TiO_2 nanoparticles, 25% rutile and 75% anatase. This method is used in a number of studies, whereas other studies do not attempt to make their results transferable.

Performance is typically quoted as a RE, which is calculated according to Equation (6), where r is RE, C_I is the inlet concentration and C_o is the outlet concentration, after interaction with the PC surface. This is a simple and intuitive metric, which is easy to compare across studies, however, as it is a relative measure, the RE calculated for a material will depend not only on the material itself but also on the test conditions, therefore REs can only be reliably compared, if the exact same conditions are used (e.g., ISO standard conditions). In this respect other metrics such as NOx removal in mg hr^{-1} m^{-2}, calculated reaction rates, or uptake coefficients may be preferable (in particular for producing models), however these are less intuitive for the reader. Regardless, a standardised testing protocol and performance metric is necessary for accurate comparison between materials. This is not currently present.

$$r = (1 - \frac{C_o}{C_I})\,100 \tag{6}$$

RE can also be defined with respect to NO concentration only, NO_2 only, or for total change in NOx, each is likely to give a different percentage removal for the same material. Therefore, it is important to differentiate between activity (overall conversion) and selectivity of that conversion toward NO_3^- on the PC surface, as opposed to conversion between NO and other gaseous NOx or NO_y species. Many lab studies simply quote RE for NO converted to other species, which does not necessarily remove NOx or improve air quality. In some lab studies, such as Khanal et al. (2021) [52], photonic efficiency is also used for comparison between materials. Photonic efficiency is defined as the ratio between reaction rate and flux of incident photons [53] and can be calculated based on the photocatalytic activity of a sample, as described in Balayeva et al. (2018) [54].

2.1.1. Impact of Physical Parameters

An understanding of how external physical parameters, such as relative humidity (RH), temperature (T), wind-speed (WS) or flow (Q), as well as irradiance and pollutant concentration, impact the RE of PCO materials is key to their effective use. It is integral to the design of pollution control systems as well as for overall assessment of their viability and for producing models. Table 1 summarises the results of a number of studies which investigate these effects.

Across the studies there is agreement that physical parameters have a significant impact on PC efficiency, in terms of both activity and selectivity, with the exception of temperature. Temperature changes within expected ambient levels were not reported to have a significant impact in lab studies. One field study conducted by Chen et al. (2011) [55] claims that as temperature increases the PC reaction rate decreases, whereas Folli et al. (2015) [56] observed an increase in RE with temperature and attribute this to higher diffusivity of pollutants to the surface. Overall it seems that temperature is not a key environmental parameter affecting performance.

Humidity

RH strongly impacts performance. Increasing humidity has been shown to reduce RE significantly, with studies typically reporting a linear fall in NOx RE when RH is increased between 10% and 80% [57–59]. For instance, NOx RE drops from 85% to below 10% in Hassan et al. (2013) [57], when RH increases from 20% to 80%. Some articles also report loss of selectivity at high RH, for instance resulting in net NO_2 production at RH > 70% in Ballari et al. (2011) [22]. This is also reported in field studies including Folli et al. (2015) [56].

Irradiance

Increased irradiance, in particular in the form of UV-A radiation, is shown to increase the performance of PC materials, as would be expected [22,57–60]. In Husken et al. (2009) [58], the relationship of both light wavelength and intensity with degradation performance is described, and separated into two regimes, where below one ‘sun equivalent’ reaction rate increases linearly with UV intensity, this is also described in previous works [61–64]. Although, in Hunger et al. (2010) [65] it is reported that at very low irradiance, <10 W m^{-2}, the dependency deviates from the linear relation. In Gallus et al. (2015) [66] (a field study) it is also suggested that in polluted environments if the level of irradiance is below a threshold value (4 W m^{-2}), this can allow pollutant build-up at the PC surface and result in rapid deactivation.

Table 1. Impact of Physical Parameters

Material	Test Setup	UV Irradiance	Inlet Concentration	Removal	T (°C)	RH (%)	Reference
Protectam FN2 (Evonik P25)	ISO standard, two flow reactors (laminar flow, ideally-mixed flow)	1.0 mW cm^{-2}	0.1–1.0 ppm NO or 0.1 ppm NO_2	NO: 75 µmol m^{-2} h^{-1}, NO_2: 50 µmol m^{-2} h^{-1}	25	50	Zouzelka et al. (2017) [67]
Anatase TiO_2 (N-400)	ISO standard photoreactor	10 W m^{-2}	1 ± 0.015 ppm NO	Mortar with 5–10% NP-400: ∼15% NO, mortar with 20% NP-400: 70% NO	25 ± 2	50 ± 5	Rhee et al. (2018) [68]
Concrete block with 0.59 wt% TiO_2	ISO standard planar reactor	10 W m^{-2}	1 ppm NO	39% NOx under ISO conditions, 45% Under optimal conditions in the field (high sun (890 W m^{-2}), low RH (40–55%), low wind (1.9 m s^{-1})). Negligible removal if dew covered or raining.	25	50	Ballari et al. (2013) [69]
Italcementi, TX-Active photocatalytic mortar	Field tests in a tunnel and ISO standard testing	0.6–1.6 W m^{-2}	50–850 ppb NOx	0–2% NOx, UVA irradiance was below the targeted values (above 4 W m^{-2}), de-activation and reduction in photocatalytic activity were recorded	-	70–90	Gallus et al. (2015) [70]
Anatase TiO_2 nanoparticles	Modified testing from JIS TR Z 0018 standard [51]	0.5–2.4 mW cm^{-2}	430 ppb NO	NOx removal 8–65% dependent on flow, RH levels and light intensity	24 ± 2	20–80	Hassan et al. (2013) [57]
Anatase TiO_2	Flow reactor adapted from ISO standard	5.8 W m^{-2}	100–2000 ppb NO	15–50% NOx, NO_2 removal negative under certain conditions	25	0–75	Martinez et al. (2011) [71]
Commercial paving stone with TiO_2	ISO standard flow reactor	0–15 W m^{-2}	0.1–1 ppm NO	0–68.4% NO, dependent on parameters	-	10–80	Husken et al. (2009) [58]
Concrete with TiO_2	'Similar' to ISO standard	2–11 W m^{-2}	0–1 ppm NO and NO_2 NO/NO_2 ratio from 0 to 1	More NO_2 produced when conditions are less favourable	-	10–70	Ballari et al. (2011) [22]
Mortar with rutile TiO_2 rods	Flow reactor (not ISO standard)	10–40 W m^{-2}	20 ppm NO	24–69 mg hr^{-1} m^{-2} NOx	-	30–70	Staub de Melo and Trichês (2012) [59]

T = Temperature; RH = Relative Humidity

Flow

Lower flow over the surface gives increased contact time between the polluted air and PC surface and so is expected to improve the RE of the surface, a number of studies investigate the effect of flow on RE between 1 and 5 L min^{-1} and observe improved RE at lower flows [57–59,71]. For instance, RE increasing from 22% to 67% when flow is dropped from 5 L min^{-1} to 1 L min^{-1} [58]. This is relevant to the prevailing wind-speed and direction when PC materials are deployed in the field.

Inlet Concentration

Similarly, when the initial concentration of a pollutant (typically NO) is increased, the RE over the PC surface drops significantly [22,58,60,71]. This effect is reported clearly in Martinez et al. (2011) [71], where an increase in inlet NO concentration from 100 to 2000 ppb, results in a drop in NOx RE from 44% to 14%, whilst NO_2 production increases, yielding an NO_2 RE of −20% at 2000 ppb (denoting overall production of NO_2). At greater concentrations the amount of NOx removed by the surface will increase in absolute terms, but the RE will drop with increasing inlet concentrations [65]. The ratio of NO:NO_2 will also impact RE for NOx as NO is removed more effectively than NO_2 by PC surfaces [55,72]. This is not well captured in most lab studies under ISO standard conditions pure NO is introduced. Whereas in the field both NO and NO_2 will be present, in a ratio depending on the prevailing conditions, but also typically in much lower concentrations than in the above mentioned studies.

Co-Pollutants

The impact of co-pollutants such as VOCs is not well described in lab or field studies. Presumably as it is difficult in the lab to manufacture pollutants mixtures that accurately represent the ambient environment (which is also variable) and that in the field the effect of co-pollutants is difficult to separate from other factors. In studies where efficiencies of the field results differ significantly from those in the lab it is sometimes claimed that high VOC levels may be responsible for this [55,73]. A mechanism for this effect would be increased competition for hydroxyl radicals and adsorption sites, and potentially poisoning of the surface with VOC reaction products [74,75].

VOCs have been shown to interact with and be removed by PC surfaces in studies on indoor air cleaning [3,31,64], that are not the focus of this article, but highlight that these surfaces are not inert to VOCs and that increased VOC concentration may inhibit NOx removal. In outdoor air a key issue related to VOC interaction with PC surfaces is the production of hazardous byproducts. In a lab study by Toro et al. (2016) [34], using a stirred tank reactor, the interaction of a mixture of VOCs with PC asphalt and concrete was investigated. When a mixture of benzene, toluene, p-xylene and tri-methylbenzene was administered over the PC surface there was uptake of all VOCs onto the surface, with varying degrees of efficiency, whilst formaldehyde and acetaldehyde were produced through degradation of the VOCs. In studies of the indoor environment significant aldehyde production is also seen, as well as the production of ketones [31]. This may be detrimental to air quality directly, as formaldehyde and acetaldehyde are carcinogens, and indirectly as they are considered O_3 precursors and may contribute to increased O_3 production and accelerate the formation of photochemical smog.

Physical Parameters Summary

In summary, the prevailing conditions at proposed sites for PC NOx abatement, particularly RH, irradiance and co-pollutant concentrations, will have a significant impact on the performance of PC materials, and may be the deciding factor in whether the surfaces significantly improve air quality, have a negligible impact, or are detrimental to net air quality.

2.1.2. Durability

There are a mixture of field and lab studies that address the issue of durability, the most comprehensive contain lab tests conducted before and after [66,76] or even during [77,78] field exposure, to quantify changes in performance over time.

Many factors contribute to the overall activity of the surface beside the active PC component and when considering overall longevity of a PC surface the structural durability of the support surface must also be appraised. The main parameters, apart from the type and weight percentage of the individual photocatalyst, that affect activity over time, are the surface roughness, colour, porosity and microstructure of the support, as well as its pH and how well distributed the PC particles are within the support [79–83].

In particular, the physical form of the structure will control the available surface for oxidation, and ratio of release:adsorption for the intermediate NO_2 produced. Concrete supports undergo carbonation over time which alters their phase composition and can affect surface area, pH and porosity, altering PC performance [79]. This may be improved with the addition of microsilica, acting as a pozzolanic material, according to Kaja et al. (2019) [79]. The method of incorporation also has an effect on durability, the main differences being that surface applications, such as spray-coating with a TiO_2 emulsion, use less active-material as the material is concentrated at the surface, whereas pre-mixing into concrete or asphalt before casting is more expensive, but, as the PC is spread throughout the bulk of the material, they remain active as the surface is worn [84]. In the case of field studies, the prevailing conditions, i.e., pollutant concentrations and rate of abrasion, will alter the lifetime of the PC surface, meaning that for instance surfaces used as part of a road surface may wear faster than those used for a pavement or bicycle lane [76], or paints used in a polluted tunnel may deactivate quickly compared with painted walls in less polluted environs [66].

It is also important to consider temporary loss of performance versus permanent wear and loss of PC material. The RE of a surface may fall rapidly after significant NOx exposure, but this can be at least partially regained by washing off nitrates from the surface, whereas loss of performance due to wearing away of the active surface or poisoning with other species is permanent. A summary of the pertinent studies is given below, including the key studies into durability catalogued in Table 2, as well as others.

In Witkowski et al. (2019) [85], lab tests were performed on a PC concrete block after 7 years of field exposure as part of a bicycle lane, however standard testing methods were not used. The test setup used a low flow (2 L min^{-1}), low concentration for a lab test (100 ppb), and defined reduction percentage by change in NO only. A 70 W and 300 W light source were used. Testing dirty samples directly from the field gave 4% NO removal, and cleaning samples only increased the NO removal to 5%, however selectivity to NO_3^-, relative to NO_2 production, did improve, increasing overall NOx removal from 1 to 4 ppb. When a stronger 300 W light source was applied to the cleaned sample, NOx removal of 34 ppb was recorded, showing that the surface was still active once cleaned and operated under idealised conditions. However, the NO_2 increases recorded demonstrate that dirty surfaces under low light conditions could have a negative impact on overall air quality. Although the paper demonstrates that NOx abatement by the surfaces was still possible, the performance could not be compared to the initial RE as this was not recorded.

Table 2. Durability.

Active Material	Test Setup	Duration	Δ Activity	Δ Selectivity	Reasoning	Reference
Commercial P25 TiO_2 and lab synthesised HT-ET TiO_2	Lab: borosilicate reactor, 30 mL min^{-1} airflow, total NO flow: 2.21 µmol h^{-1}, lamp $\lambda_{max} = 365$ nm, irradiance: 9 mW cm^{-2}	18 h	NO conversion fell from 100% to 68%	Conversion of NO to NO_2 increases rapidly from 0 to 50%	HNO_3 and NO_3^- formed on surface deactivate TiO_2	J. Araña et al. (2019) [72]
'Nano-TiO_2'	Lab and field: bicycle lane in Poland and novel lab setup, 100 ppb inlet NO, 70 and 300 W lamps, flow of 120 L hr^{-1}	7 years	Only measured after wear, 4–45% NO RE depending on test conditions	NO_2 production was equal to NO removal for dirty samples under 70 W light	TiO_2 still present in samples after 7 years	Witkowski et al. (2019) [85]
Ultrathin BiOBr/BiOI	Lab: continuous flow reactor	360 min	Negligible change	Increased NO_2 production as NO_3^- on surface increases	Adsorbed NO_3^- alters the surface environment, changes oxidation process	Shi et al. (2019) [86]
Concrete with TiO_2 and activated carbon spray coating	Lab: stainless steel reactor, RH 48–53%, T = 25 °C, light intensity 0.3 mW cm^{-2}	'multiple tests', followed by regeneration and accelerated wear from polishing	Quoted for NO and NO_2 separately, ranging from 78.2% to 25.84%, reduced RE after repeat tests, partially regained after regeneration, and further lowered after wear	-	Regeneration by washing with water removes nitrates from the surface. Some RE capability is retained after wear as the coating is able to penetrate the surface	Chen et al. (2011) [55]
Asphalt and concrete with spray TiO_2 coating	Lab and field: tested according to JIS R 1701 [51] in the lab and with nitrate extraction method on pavements in the field	5 months of 'light wear'	Loss of 50% in RE over 2.5 months, calculated lifetimes of 6–11 months for concrete and 10–16 months for asphalt	-	Sprays coatings on the surface are subject to wear	Osborn et al. (2014) [77]
Blocks of Portland cement containing pozzolanic material with anatase or rutile TiO_2 at varying thicknesses	Lab and field: lab studies conducted on blocks before and after 1 year field exposure	1 year of wear on roads and pavements	Loss of 79–87% of initial RE after 1 year, 21–29% of initial RE regained after washing	-	The blocks showed considerable loss of PC area due to abrasion and wear. Blocks with a thicker PC layer are recommended. Textured surface increases initial RE but is more susceptible to wear	Staub de Melo et al. (2012) [76]
Concrete blocks with 0.59 wt% TiO_2 content	Field: paving blocks in residential street	20 months cumulative for all materials	Activity lost after 2.5 months and then 11 months	-	Coating lost due to normal wearing via vehicles, weathering, and deposition of soils	Ballari et al. (2013) [69]

In J. Araña et al. (2019) [72], the temporary effect of the build-up of nitrate on the PC surface is investigated for both P25 and a novel lab synthesised TiO_2 catalyst (called HT-ET). The study is not conducted under ISO conditions, just 20 mg of powdered catalyst is used in each test, under a total flow of 30 mL min^{-1}, containing 2.21 µmol h^{-1} of NO, with the sample irradiated at 9 mW cm^{-2}. After 18 h under these conditions NO conversion fell from 100% to 68% and selectivity to NO_2 increased from 0 to 0.7 for the conventional TiO_2 sample, meaning that although significant activity in terms of NO removal remained for the 18 h period, significant removal of overall NOx was only evident in the first few reaction hours. Similar poor results for P25 are reported in other studies [87,88]. This shows that even without the presence of other pollutants, dirt, or wear caused by abrasion the selectivity and activity of PC surfaces will fall following exposure due to the build of nitrate products, and shows that NO_2 is not efficiently removed by these surfaces. Although nitrate will to some extent be washed off by rainfall in field environments.

In a 2014 study by Osborn et al. [77], which aimed to quantify the durability of a PC surface made by spraying a TiO_2 suspension on to asphalt or concrete, lab tests were conducted using the JIS R 1701-1:2004 standard [51] and a nitrate extraction method, a correlation factor linking the methods was then identified. Afterwards, samples were installed in the field for 5 months and monitored via nitrate extraction each month. The results were used to calculate regression models representing decay of the surface RE over time. The most rapid loss of performance was seen in the first month and service lives of 6–11 months for concrete and 10–16 months for asphalt, when used as a pavement surface, were calculated.

Application of PC paint in tunnels is seen as a promising scenario for their use due to the high surface area to volume (SA/V) ratio, and possibility of applying consistent high UV irradiance, as described in Section 2.2.3. However, during the 2015 field study in the Leopold II tunnel, Brussels (described in Section 2.2.3 and in [66]) significant passivation of the surface and decrease in selectivity following field exposure was observed. Lab tests confirming this are described in Boonen et al. (2015) [89], a reduction of NO removal activity by a factor of 12 was recorded, together with a 50% increase in NO_2 yield from NO oxidation. This is attributed to the deposition of particles, e.g., soot, and adsorption of semi-volatile organic compounds on to the surface. Activity could only partially be restored by rinsing with water and prolonged exposure to UV light in clean air. The study recommends that, as well as the site-specific modelling and field testing recommended by other studies prior to making large-scale installations, specific testing should be conducted to identify the rate of deactivation under the prevailing conditions in individual tunnels. This could be performed by introducing polluted tunnel air to the same photo-reactor used in lab studies, with UV illumination at the same level as expected in the tunnel [89].

The 2013 study conducted by Hassan et al. [57] investigates lab and field performance of TiO_2 photocatalytic coatings under a range of conditions, it is catalogued in Table 1. The durability of surface coated asphalt is also investigated through an accelerated wear test using a loaded wheel. After 20,000 cycles of the wheel there was an average drop of 68% in NOx RE. The authors note that the test resulted in significant distortion of the material that may have been excessive relative to a field deployment.

In the combined field and lab study by Chen and Chu (2011) [55], where a TiO_2 coated highway was investigated, rapid build up of HNO_3 and partially oxidised intermediates on the PC surface was observed in lab experiments, this was evidenced by a decline in removal rate (from 58.5% to 34.3% for NO_2) and a visible change in the material colour from white to yellow/brown after repeated exposure tests. The performance of the surface was partially regained after washing (rising to 43.0%), indicating that performance can be partially regenerated by washing or rainfall. Artificial wear induced by polishing the surface was also investigated. After polishing, NO_2 RE dropped from 58.5% to 25.8%, suggesting that the amount of wear in a specific environment is also key to durability estimates. However, in this study neither the level of cumulative exposure after the repeat experiments, or a quantitative assessment of the amount of wear is given. Standard ISO testing was not used, instead a reactor was built that could have an automobile exhaust connected to the inlet to provide pollutants (setup described in Chen and Liu (2010) [90]), this is a more realistic testing method than the ISO standard, however inlet concentrations are not reported in the study.

In the 2012 study by Staub de Melo et al. [76], concrete blocks with TiO_2 incorporated by casting into the top-layer, were tested for RE before and after one year of exposure in the field. Significant reduction in efficiency after the field installation was observed, the blocks from the road section had an average drop in efficiency for NOx degradation of 87 ± 7% and for the blocks from the pavement an average reduction of 79 ± 8%. This could be partially regained by washing, leading to 21 ± 5% and 29 ± 6% recovery in RE for the road and sidewalk, respectively. This demonstrates that wear is a significant issue at this timescale and that although some loss in efficiency, resulting from dirt or partially oxidised products covering the surface, is reversible; other wear, due to physical loss of the mortar and exposing aggregates, is irreversible. This study also demonstrated that materials with a greater surface roughness and texture can yield greater initial RE, but are also more susceptible to wear, especially if used in roadways. PC layer thicknesses of 3–10 mm are used in this study, it recommends that greater thicknesses are used to increase durability.

In the field study conducted by Fan et al. (2018) [84], asphalt coated with a TiO_2 suspension showed visible wear after two days of tire-abrasion, durability was improved somewhat by heat-treating the surface, although the effect of this on RE was not quantified.

In a pilot study in Antwerp by Boonen and Beeldens (2013) [37], paving stones were tested in the lab after 5 years in the field and still maintained some activity for removal of NO, although it is not clear what fraction of their initial activity was maintained [12,37].

In the 2013 field study by Balleri et al. [69], an effective (19% NOx removal) area of TiO_2 concrete lost all efficiency after 2.5 months in the field. A second 'more durable' coating was added, which lasted for 11 months before losing all RE, but the changes in the coating to increase durability were not disclosed.

In the 2019 study conducted by Jiménez-Relinque et al. [78] (described further in Section 2.2.1), a novel method for measuring the PC RE of materials, in situ in the field was developed [91]. This allowed for quantitative assessment of changes in RE over time, in the field. During the 17 month period, cement slurries containing TiO_2 and coated on to asphalt, as well as TiO_2 cast into concrete tiles were shown to retain activity, whereas TiO_2 emulsions coated onto asphalt lost all activity. This again demonstrates that durability can drop significantly over month timescales but also that substrate material choice and method of incorporation may be key to the longevity of performance. This is discussed further in Section 2.1.3.

Durability Summary

A number of the durability studies do not clearly quantify change in efficiency relative to time or exposure, but merely show 'some removal' after a time length of exposure. From the studies available that make quantitative comparisons of performance, before and after field deployment or exposure to NOx in the lab, it is clear that durability is an issue for these materials and that their lifespan seems to be on the order of months rather than years, and in some cases days [69,84]. There are both short-term losses in performance, due mainly to nitrate build-up, that are at-least partially reversible, and longer term, irreversible, loss of performance due to abrasive wear and poisoning.

2.1.3. Material Improvements

In 2007 Hunger and Brouwers made a comparative study of the available commercial concrete products containing TiO_2 [92]. They included products from the two companies that hold patents concerning the use of TiO_2 in paving blocks in Europe, Mitsubishi [93] and Italcementi [94]. The tests were conducted under conditions corresponding to a draft version of the ISO standard, as well as alternative test conditions deemed more relevant to ambient use. In total, 12 samples were tested and under the conditions used ($Q = 3\ L\ min^{-1}$, RH = 50%, NO = 1 ppm, I = 10 W m^{-2}), which represent optimum laboratory conditions, there was large variability between the materials. The average recorded NOx REs range from 2.8% to 44.6%, showing that there are large differences in efficiency between commercial products, and proper selection will be key to a successful installation. This testing shows that even under idealised lab conditions current commercial materials are not able to offer consistently high REs, this performance will also be expected to drop under less optimal ambient conditions, and with prolonged field use. This, and the negligible abatement reported for many field studies shows the need for further improvements to PC surfaces. In lab studies conventional TiO_2 is shown to be unselective when oxidising NOx and can lead to an increase in NO_2 concentrations, this led a 2016 review of photocatalytic concrete to claim that more research is needed in both the photonic efficiency and selectivity of TiO_2 based photocatalysts to make them viable [38].

Research into PC development can broadly be split into, doping of the TiO_2 itself, and optimising the TiO_2 support material or method of incorporation. Recent, pertinent studies are documented in Table 3. These studies aim to make improvements to the known weaknesses of TiO_2 for the oxidation of NOx. Key areas for improvement are, selectivity to nitrate (particularly at high humidity), resistance to poisoning, and activity under visible light. Durability of the material is also a concern.

The band gap of TiO_2 is relatively large (3.0–3.2 eV) and therefore it is active under UV light below 400 nm in wavelength, which appears at low intensity in the ambient urban environment. Therefore, a shift in the band gap to a lower energy, within the visible range (which accounts for 43% of incoming solar radiation, compared with 3–5% for UV), that is still great enough to initiate the oxidation of NOx, would increase the activity of the surface under ambient conditions [95,96]. A large amount of research has aimed at increasing the efficiency of light harvesting under solar excitation, whilst preserving or improving the fraction of electron hole pairs that do not recombine [97].

Doping

Doping the TiO_2 surface, or forming a nano-composite with other species, such as noble metals, metal-oxides and carbon, is generally aimed at increasing the activity of the material, chiefly through shifting the band gap towards the visible region and preventing electron/hole recombination. There has been extensive research into this, with studies investigating doping with Fe [96,98,99], Fe_2O_3 [100], Cu [98] , Sn [101], Zn [102], Zn-S [103], Au-N [104], Al_2O_3 [105], Pd [88,106], Pt [107], Pt/Au [108], Ag [109,110], g-C_3N_4 [111,112], graphene [113], Sn and Ce/Mn-graphene [114], other forms of carbon [53,115] and minerals from clay [116]. Many of these have previously been summarised in tables in Martinez et al. [98,101]. Studies have also reported improvements to selectivity and visible light activity resulting from co-doping with Nb,N [117] and W,N [118–120]. Doping with Pd specifically is claimed to have a large range of benefits, including increased selectivity and resistance to nitrate poisoning, as well as shifting the band gap towards visible light, making it an attractive prospect [106,121,122].

Table 3. Material Improvements

Material	Test Setup	Dopant	Support	Method of Incorporation	Δ Activity	Δ Selectivity	Reasoning	Reference
BiOX Mortars	ISO	-	1:3 ratio of sand to Portland cement	Powder incorporated in cement at 10 wt%	BiOX Mortars: 7.6% NO, 4% NO_2, P25: 4.3% NO, 1% NO_2	BiOX Mortars: 83% P25: 24%	Presence of oxygen vacancies together with a strong oxidation potential	Nava-Núñez et al. (2020) [123]
P25, KRONOclean 7000 and lab synthesised SiO_2-TiO_2 composite	ISO	C	Microsilica (pozzolanic material) in Portland cement	PC as 5 wt% of the binder	Microsilica addition imporoves post-carbonation activity	Microsilica addition imporoves post-carbonation selectivity	High SSA, maintained after carbonation due to high pH	Kaja et al. (2019) [79]
Blue TiO_2	ISO	Fe and Cu	Sample disk	Hydrothermal-assisted sol-gel method	NO oxidation: Blue Fe-TiO_2: 70% Blue Cu-TiO_2: 57.71% Blue TiO_2: 54.57% P25: 34.96%.	NO_2 selectivity: P25 TiO_2:36.08% Blue TiO_2: 21.7% Blue Cu-TiO_2: 4.3% Blue Fe-TiO_2: 11.65%	Oxygen vacancies and smaller band-gap	Martinez-Oviedo et al. (2020) [98]
Commercial TiO_2	Continuous flow reactor	g-C_3N_4	Portland cement	Suspension Mixed into cement before casting	2% g-C_3N_4 addition increases NOx removal from 37.5 to 227.3 μmol m^{-2} h^{-1}	-	Smaller band gap	Yang et al. (2019) [124]
KRONOClean 7050 TiO_2	ISO	-	Portland cement	Liquidized powder incorporated in cement	360% NOx removal compared to plain cement	-	Addition of TiO_2 alters microstructure as well as adding PC effect	Jin et al. (2019) [125]
P25 TiO_2	Continuous flow reactor, similar to ambient conditions	Sn	Sample disk	Dispersed in acetone and distributed on a sample disk	Blue Sn-TiO_2: 72% NOx removal, compared with 42% for P25	Blue Sn-TiO_2: 29.42% NO_2 formation, compared with 125.19% for P25	Multiple reasons including: band gap reduction, increased SSA, and efficient e^-/h^+ separation	Martinez-Oviedo et al. (2019) [101]
KRONOClean 7000 TiO_2	Chamber test	C	Asphalt	PC powder suspended in water, sprayed onto asphalt, and heated	For 2 g m^{-2}, after 3 h C-TiO_2: 90% NOx RE, compared with 55% for P25	-	Smaller band gap	Fan et al. (2017) [126]
TiO_2	RhB solution	-	CNT and rGO composite	Solvothermal method	1.5× the rate of pure TiO_2	-	Decreased e^-/h^+ recombination, increased hydroxyl content at surface	Huang et al. (2018) [115]

Table 3. *Cont.*

Material	Test Setup	Dopant	Support	Method of Incorporation	Δ Activity	Δ Selectivity	Reasoning	Reference
Aeroxide P25 TiO$_2$, Evonik	Continuous flow reactor	V and Fe	Selection of cement matrices, including high alumina cement (HAC) and air lime	Binder:aggregate ratio of 1:3 and TiO$_2$ as 0.5, 1 and 2.5 wt% of binder	Fe showed better improvement than V, even though V harvested more visible light	High NO selectivity with low release of NO$_2$ for air lime and HAC systems	Selectivity values for NO degradation were high (>60%), yielding calcium nitrates that are easily removed from the photocatalyst surface, thus enhancing the PCO reaction	Pérez-Nicolás et al. (2017) [96]
Range of commercial TiO$_2$ products	Specific ‘PHOTONSITE’ setup, validated against ISO standard	-	Asphalt and concrete tiles	Slurries, emulsions and precast into bulk	Faster RE loss on asphalt than concrete, RH of preceding days impacts RE	-	Substrate hygro-inertia alters acute impact of RH	Jiménez-Relinque et al. (2019) [78]
Commercial anatase, Evonik Aerodisp W740X	Flow reactor adapted from ISO standard	-	Glass and mortar	Coating made with acrylic binder	-	Significantly lower selectivity on glass, also falling with exposure	On mortar NO$_2$ produced is absorbed, meaning less competition for adsorptive sites	Martinez et al. (2011) [71]
Commercial TiO$_2$ and carbon doped TiO$_2$	ISO	Carbon	Concrete with varying surface roughness	Dry powder or suspension	Increased RE for: rougher surfaces, doped TiO$_2$, suspension method and finer powders	-	Rougher surface improves deposition, increased SSA and distribution improve uptake, dopants shift absorbance toward visible	Husken et al. (2009) [58]
Nanostructured TiO$_2$	ISO	Atomically dispersed Pd	Glass fibre	Annealing and spray drying	Increase in NOx RE by 10 times with 1 wt% Pd, relative to P25	-	Single Pd atoms on TiO$_2$ dominate NOx removal	Fujiwara et al. (2017) [106]
Fe$_2$O$_3$/TiO$_2$ nanocomposite	Similar to ISO but 100 ppb NO and 0.3 L min^{-1}	Fe$_2$O$_3$	-	‘Original low-temperature plasma assisted strategy’	Activity of composite lower than Degussa P25	63% for composite, compared with 25% for P25	Nanocomposite has a lower band gap and improved electron-hole separation	Balbuena et al. (2016) [100]
Aeroxide P25 TiO$_2$, Evonik	ISO	g-C$_3$N$_4$ and CaCO$_3$	-	Suspended in water, then annealed	5 times greater than pure TiO$_2$ under visible light	Alters with composition, moved DeNOx index from negative to positive	CaCO$_3$ reduces NO$_2$ production, composite is synergistic and shifts bandgap toward visible region	Papailias et al. (2017) [112]
P25, anatase and rutile TiO$_2$	Self-designed flow reactor	-	Concrete with varying cement, glass and sand aggregrate ratios	Wet-mixed, compacted and cured	NO removal in mg hr^{-1} m^{-2} increased with porosity and glass content	-	Porosity increases the area available for reaction and glass increases transmission of light	Poon and Cheung (2007) [80]
Aeroxide P25 TiO$_2$, Evonik and Hombikat	ISO	-	Zeolite ZSM-5	Sol-Gel synthesis	Composite TiO$_2$: 41% NO conversion, P25: 45%	Composite TiO$_2$: 19% NO$_2$ selecticity, P25: 65%	Zeolite gives extra available SSA and act as sink/reservoir for HNO$_3$	Tawari et al. (2016) [127]

There is promising work in this field but almost none of the modified materials have actually been deployed in field studies, this is partly due to them being novel, recently developed materials, but also because doping with noble metals such as Pd, Pt, Au and Ag may make materials too expensive for use at scale. To minimise additional costs sub-nanoclusters and even individual atoms can be dispersed on to the PC materials to achieve the greatest possible surface availability-to-cost ratio [106]. However, doping with more abundant materials such as C or Fe is still more likely to produce a viable product if successful, for example one of the only doped TiO_2 material to be successful commercially and to be used in a field study is KRONOclean 7000, a commercial C-doped TiO_2 material [126]. Carbon-doped TiO_2 was used in a field study conducted by Ballari et al. (2013) [69], and 19% RE for NOx was observed (if only the daytime was considered), this is one of the highest recorded REs for a field study where street paving materials are considered, which indicates that using this kind of doped TiO_2 may improve field results. However, there are issues relating to durability and analysis in this study, detailed in Section 3.5. Other lab studies have confirmed the benefits of doping with carbon, including improvements to the loss of selectivity typically seen at high humidity and high co-pollutant concentrations [128], as well as improved RE under visible light [53]. Conversely in a small field-trial conducted by Fan et al. [84] C-doped TiO_2 had an impact on NO but did not achieve significant NO_2 removal. Therefore, it is not yet entirely clear how material improvements from lab studies translate to the field.

Support Material

The support material is shown to have a significant impact on overall performance, meaning that the same TiO_2 photocatalyst may perform far better over time when applied to concrete compared with glass or asphalt, and when applied with a different method of incorporation [58,71,78]. Improvements related to the support material are typically in the fields of durability, activity and selectivity.

For instance, the support can affect activity by having a rougher surface that improves deposition rate [58] (although this may affect durability), or through surface area and transmission improvements. For instance, through the inclusion of different aggregates such as glass chips, that increase light transmission [80], or pozzolanic materials in concrete that preserve porosity [79].

Selectivity can be greatly influenced by the support material. With the optimal support, the NO_2 production which occurs during NO oxidation, can be suppressed. For example, concrete can be produced with high specific surface area porosity in the correct size region to adsorb NO_2 and so suppress the NO_2 produced when large amounts of NO are oxidised [79,96]. Other materials with high porosity, such as zeolites can also serve this purpose [127].

The pH of concrete can also be tuned through the use of different aggregate mixtures and with additives such as lime, alumina and $CaCO_3$ [82,96]. Adding basic character to the surface facilitates increased oxidation of NO_2 to nitrate, and thereby improves the selectivity of NOx PCO [79,112]. In these respects concrete is superior to asphalt and far superior to glass [71,78].

The application method or method of incorporation is also important, with one study showing significant loss of activity for emulsions on asphalt over time, relative to fairly constant removal for cement slurries on asphalt and TiO_2 incorporated into concrete tiles [78]. In a separate study, Husken et al. investigated the use of suspensions, which improved dispersion relative to a dry powder method, as well as using finer TiO_2 particles, greatly improving activity for the same weight percentage of TiO_2 [58]. The dispersion of TiO_2 through the support material, relative to aggregation or flocculation will alter the available surface for reaction and hence the activity, this is yet another parameter that must be considered when producing a PC surface and will depend on the initial size of TiO_2 particles and method of incorporation, as well as chemistry between the TiO_2 and support [40,129].

Other Catalysts

Overall titania remains the catalyst of choice in most cases, but beside doped TiO_2 there is also growing interest in other materials entirely, such as BiOX mortars [123]. Other metal-oxides [52], perovskites and semi-conductor graphene have also been investigated, as well as composites of different catalysts, a number of these are listed in Byrne et al. (2018) [2], but they have not yet been the subject of large scale field trials.

Material Improvements Summary

Detailed examination of all the individual studies documenting material improvements is beyond the scope of this work, but it is clear from the assembled studies that improvements are continually forthcoming. There is evidence that the doping of TiO_2 can improve its performance in key areas but also that the correct support material and method of incorporation may be as important as the selection of active material in many cases. Most of the improvements to the active material are untested in field environments however.

2.2. Field Results

As mentioned previously, the field studies in this area can be split into trials taking place on (1) streets, where the PC material is the actual pavement or road surface (e.g., concrete blocks or asphalt), (2) walls, where PC active paint is applied to surrounding buildings or model street canyons and the PC surface is predominantly vertical, and (3) enclosed spaces, this is mainly tunnels and car parks. Typically paints are also used but the enclosed spaces are a particular subset of field-trial due to the different conditions imposed, chiefly artificial UV light instead of sunlight, the lack of rainfall, and potential for greater pollutant concentration build-up.

A number of the field studies in this area were conducted as part of two EU funded projects: 'Photo-catalytic Innovative Coverings and Applications for De-pollution Assessment' (PICADA) and Photocatalytic remediation Processes on Air Quality (PhotoPAQ) [24]. The PICADA trials report significant REs of up to 82%, but their results are considered questionable due to the use of high SA/V ratios that are not realistic in actual urban environments, as well as other issues discussed in Section 3.5 [23,24,70]. The work by PhotoPAQ is considered more comprehensive and typically reports low or negligible NOx abatement, the studies are described below. As with the lab studies the range of methods used for quantification of abatement make the field studies difficult to compare.

The LIGHT^{2}CAT industry-academic collaboration was a 5 million euro project which ended in 2015 [130], and had the aim of developing new highly efficient PC surfaces activated by visible light, improvements appear to have been made in the selectivity and activity of TiO_2 under visible light through co-doping [117–120]. The only published field study resulting from the project (Copenhagen 2015 [56]) was an initial study of conventional TiO_2 and does not report effective NO_2 abatement as the catalyst is not selective to nitrate, and only NO concentrations were lowered. The results were also used to illustrate the dependence of PC surfaces on UV irradiance and to model in what period of a year a surface can be effective at a specified latitude [131]. The LIGHT^{2}CAT project summary report [130] reports NOx abatement of 5–20% based on their field studies in Copenhagen and Valencia using their doped TiO_2 surfaces, which is in line with other studies, however it is claimed that this NOx abatement is made up of a higher fraction of NO_2 removal relative to previous studies. In the internal report produced for the Danish Technological Institute (DTI) more analysis of the individual studies is given [132].

2.2.1. Streets

The studies described in this section are tabulated in Table 4.

Table 4. Streets.

Location	Test Setup	Light	Removal	WS	T	RH	Comment	Ref
Copenhagen, Denmark	2 × 200 m stretches, each 100 m with and 100 m without TiO_2, sampling at 2 m height	Sunlight, 0–1500 kJ m^{-2} day^{-1}	22% NO, but negligible for NO_2	-	18–25	25–83	NOx conversion decreases with RH, increases with T, selectivity is an issue	Folli et al. (2015) [56]
Sheung Shui District, Hong Kong	30 × 3 m, 15 m coated, 15 m uncoated	Sunlight	100% NOx in 1.5 h in lab, NO_2 removal negligible in field	-	-	-	NOx source: two cars driven continuously, poor selectivity and durability	Fan et al. (2018) [84]
Hengelo, Netherlands	150 m coated street, 100 m control street	44–745 w m^{-2} with UV-A 3% of total	19% NOx (daytime)	0.6–2.69	2.4–27.9	37.7–86.6	Sampled at 5, 30 and 150 cm, rapid decay in performance, negligible removal when wet	Ballari et al. (2013) [69]
Madrid, Spain	Pilot scale, 9 materials tested over 17 months, using a specially developed 'PHOTONSITE DEVICE'	Ambient or 10 W m^{-2} from 365 nm LEDS	1–32% NOx	3 L min^{-1}	-	25	Lab tests also conducted under ISO conditions to validate results, conclusions are that the RH of the preceding days is key to RE,due to hygro-inertia. Recorded overall degradation in RE over time, more on asphalt than concrete	Jiménez-Relinque et al. (2019) [78]
Tsitsihar, China	Experimental area of road divided into test and control sections, with synchronised sampling, 0.5 m from surface	Sunlight	12.35–24.1% NOx (daytime)	<0.8	-	-	Far lower RE recorded for outdoor than indoor (lab) tests. Different rates in summer and winter	Chen et al. (2011) [55]
Bergamo, Italy	PC concrete blocks in central Bergamo street, 500 m long, 12,000 m^2 active area. 2 measurement campaigns, each two weeks	Sunlight	26–66% NOx RE	-	-	-	Analysis is contested in Gallus et al. [70] and Flassak and Bolte [133,134]	Guerrini and Peccati (2007) [135]
Bergamo, Italy	5 × 5 × 53 m, Walls and ground coated with Italcementi, TX-Active	Sunlight, UV-A up to 40 W m^{-2}	≤2% NOx RE	<1 inside, 1.5 above	-	-	SA/V Ratio: 0.6 m^{-1} Material did not decay after field test	Gallus et al. (2015) [70]

WS = Wind-speed [m s^{-1}], T = Temperature [°C], RH = Relative humidity [%]

Copenhagen

Folli et al. [56] conducted a study of PC concrete paving in central Copenhagen (2015). The study compares control and active sections of pavement, each 100 m long, on either side of the same street. The active concrete paving stones contain TiO_2 in the their uppermost 10 mm of surface and at a concentration of 40 kg m^{-3} in this layer, they were supplied by Starka Betongindustrier. The blocks were shown to be active for NOx removal in the lab prior to installation, although not with ISO standard testing. As well as comparison between control and active sections (over a 14 month period), NOx measurements began 2 months before the installation of the paving to establish a blank. A monthly average off 22% NO RE was recorded during summer months when comparing between the active and control areas. However, a significant drop in NO_2 was not recorded. A maximum abatement in NO was recorded at noon during the summer solstice, which resulted in 45% NO removal and consequently a 30% overall NOx RE. This study seems to have a robust design, and indicates that PC road surfaces can physically affect ambient NOx concentrations, but overall demonstrates that PC surfaces must be selective to nitrate and active towards both NO and NO_2 to provide tangible air quality improvement.

Hong Kong

The study by Fan et al. conducted in 2018 [84], investigates NOx removal by asphalt which was made photo-active by spraying with a carbon-doped TiO_2 emulsion and then heat treating. The material was first tested in the lab, this took place in a chamber setup, not under ISO standard conditions, but a comparison to conventional P25 TiO_2 was made. At the same loading of TiO_2 (2 g m^{-2}) the C-TiO_2 surface removed 88% of NOx in a chamber after 3 h, whereas the P25 removed 50%. Controlled testing of the material was then conducted in situ over 30 m of paved street, split into control and test sections (each 15 m). Testing was conducted during sunny days and two vehicles were driven back and forth as pollution sources, the distance of the monitors from the surfaces is not mentioned. The results of the field measurements show that NOx levels are significantly lower over the test than the control section (this was not quantified but appears to be $\sim$15%), but there was not a significant difference in NO_2 levels. Low durability of the coating is also noted, and after just two days wear from the vehicles the TiO_2 that is not in the troughs of the asphalt surface is visibly worn off, heat-treating the asphalt to improve the binding of TiO_2 was tested and it is claimed to improve the durability, but this is not quantified.

Hengelo

Ballari et al. (2013) [69], conducted a full-scale test of PC concrete blocks in Hengelo, Netherlands. The study compared a 150 m active street with a 100 m control street paved with standard blocks. The monitoring period exceeded one year, but with only 26 days of measurement. As well as monitoring NOx concentrations, [O_3], T, RH, WS, WD, traffic intensity and UV irradiance were measured. Lab tests (ISO standard) were also conducted on the blocks before and after installation. Overall this appears a comprehensive and well-designed study. Initial tests conducted with pre-cast photocatalytic concrete blocks from Struyk Verwo Infra (installed in November 2009) did not show significant NOx removal. Subsequently the street was sprayed with an additional coating of C-doped TiO_2 (from Kronos International) in May 2010, the active street then initially displayed NOx REs of up to 45% under ideal conditions and at a daytime average of 19%. The performance quickly dropped however and after 2.5 months was negligible. The study attributes this to weathering, wear and/or solids deposited on the surface. A second coating was then added that lost its efficiency at a lower rate but was also found to have negligible removal after 11 months. At first glance this study demonstrates that significant removal is possible (with doped TiO_2), but also highlights issues with TiO_2 selection, application and durability. The testing method is further discussed in Section 3.5.

Madrid

The study conducted by Jiménez-Relinque et al. [78] in 2019 aims to 'bridge the gap' between lab and field studies by developing a portable device for evaluating PC activity, that can record REs in situ in the field, but has been validated against an ISO standard lab setup [91]. This type of study is different to typical field studies as it does not measure the impact of the PC surface on the ambient NOx levels in the surrounding area, however it can give quantitative information about the change in efficiency of a surface in the field over time, as well as testing under actual ambient conditions. Another attempt to make this type of bridging study was also conducted by Suarez et al. (2014) [136], but this is the most recent and comprehensive. In the study, 9 PC materials were tested over a 17 month period. The results show a significant loss in NOx RE over the 17 month period for TiO_2 emulsions coated on to asphalt, whereas cement slurries on asphalt and concrete tiles had relatively constant activity over time. Separate from the steady decline in RE for some materials, variation in activity over the period for all materials was also strongly associated with changes in the humidity level of the support, not the current RH in the air. This meant that activity was dependent on the RH of the preceding days, the number of days that would influence RE depended on the hygrometric inertia of the materials, for the asphalt the mean RH of the previous 28 days would determine the substrate humidity, whereas this was just 3 days for the concrete tiles. This information is important to incorporate into future models.

Tsitsihar

In 2011 Chen and Chu [55] investigated concrete spray-coated with TiO_2 and C-TiO_2 for NOx abatement using lab and field experiments in Tsitsihar, China. The lab component, focusing on durability, is described in Section 2.1.2. In the lab high REs were recorded for both NO (up to 78.2%) and NO_2 (up to 58.5%). In the field component of the study a road is divided into test and control sections, with synchronised sampling at 0.5 m from the surface. Concentrations were recorded with adsorbent tubes and the concentrations were measured over a 3 month period, meteorological parameters and traffic intensity were also recorded. The RE for NOx in the outdoor tests was far lower than the lab tests, with a range 12.35–24.1% for NOx removal at the different sites, including daytime hours only, the results are not separated into NO and NO_2 removal. The decreased efficiency in the field test is attributed mainly to the presence of VOCs that inhibit NOx removal [74,75].

Bergamo—Model Street Canyon

A study of NOx (as well as VOC, O_3 and PM) abatement in a model street canyon ($5 \times 5 \times 53$ m) was conducted by Gallus et al. [70] as part of the PhotPAQ project in 2015. Reference and active model street canyons were built with the same dimensions and compared during the day and night to quantify the PC activity of the active canyon during the day time. The active canyon was coated in PC mortar (TX-Active Skim Coat Boosted) from Italcementi. A full raft of environmental parameters were measured, as well as the pollutants mentioned above, using a range of instruments. Laboratory studies of the materials were also conducted pre- and post- field installation, this was not done using ISO standard conditions, but was performed under realistic conditions for real-world use. The experimental design as well as the data analysis and quality assurance seem robust. In initial lab testing the material appeared highly active for NO and NO_2 removal, the lab results are given as uptake coefficients and uptake velocities in the study. However, in the field component no significant PC oxidation of NOx was observed (or remediation of any of the other pollutants). An upper limit of <2% removal was calculated from the day:night comparisons between the reference and active canyons. Due to the passivation of PC surfaces observed in other studies conducted in polluted environments [69,89], repeat lab tests were conducted on the PC material from the field site, but no loss of efficiency was seen after the campaign, this is expected as there was relatively short exposure (3 weeks), at low pollutant concentrations compared with the other field studies mentioned. The low

RE could also not be explained by having a low SA/V ratio as the model street canyon had a relatively high SA/V ratio of 0.6 m^{-1}. The article argues that 2% is a reasonable NOx abatement for this type of PC technology and that many other studies should have their data re-evaluated to this level. This is discussed in Section 3.5.

Bergamo—Concrete Paving

A field trial of a pavement made from PC concrete blocks was conducted in Bergamo by Guerrini and Peccati of the Italcementi group in 2007 [135]. The blocks were installed along a 500 m long section of road, creating an active surface area of 12,000 m^2. NOx levels were monitored, together with relevant atmospheric parameters and vehicle frequency, for two, two-week periods, one in November 2006 and one in January 2007. These were compared with concurrent measurements on a control street without active PC material, from preliminary measurements the areas were shown to have similar NOx levels. Measurements were conducted at 30, 100 and 180 cm from the surface, during the different measurement campaigns. In the first campaign daytime differences in NOx of 26–56%, between the active and reference streets (measured at 1 m) were reported. In the second week an average 30% difference at 30 cm from the surface and 20% at 1.8 m was reported, again for the daytime only (8:00 a.m.–18:00 p.m.). The lower RE in the second week is attributed to unfavourable meteorological conditions and the presence of heavy trucks.

The study reports significant NOx abatement and appears to measure all of the appropriate parameters needed for such a field study. However, the results are contested and the study design has been drawn into question, due to the measurement of NOx close to the PC surface, and significant distance between active and control sites, which can lead to greater uncertainties due to differences in pollution emission and dispersion [70]. NOx abatement was recalculated by Bolte and Flassak, and taking into account the differences between sites it was reduced to 4–14% [133,134]. It is argued by Gallus et al. [70] that the lower limit of 4% should be reduced to <2% taking into account diurnal averages and transport limitations, which would put this study in agreement with a number of others claiming NOx removal below 2% [66].

Streets Summary

In their 2010 study Hunger et al. [65] conclude that at the time no field study of PC pavements reported a verifiable NOx abatement solely from the action of the pavement. This was due to shortcomings in the studies which include, insufficient characterisation of pollution levels before intervention, sampling distance from the PC surface, lack of simultaneous measurement in reference and active areas, and poor choice of location and/or measurement of environmental parameters. The study conducted by Ballari et al. in Hengelo Netherlands, (2013) [69] was designed to remedy this by meeting the test criteria in terms of measuring a full raft of environmental parameters (T, WS, WD, RH, air pressure, light, traffic volume and ozone concentration), as well as NOx over more than 12 months, covering all seasons, at both active and reference areas, and at a range of heights from the pavement. Therefore, it can be considered as one of the most comprehensive studies on record. However, it reports rapid decay of the surfaces efficiency over time and the data analysis that produced the 19% RE is questionable (discussed in Section 3.5). Therefore, the evidence from the street studies is not convincing in terms of significant NO_2 removal.

2.2.2. Walls

The studies investigating the effectiveness of vertical surfaces for PC NOx abatement are compiled in Table 5 and summarised below.

Table 5. Walls. All studies lit with natural light and irradiance not quantified, except for [137].

Location	Test Setup	Removal	WS	T	RH	Comment	Reference
Gyeongbu expressway, Korea	TiO_2 paint added to retaining wall, coated section: 150 m × 1.9 m, control section: 200 m × 1.9 m	13% NOx (daytime)	1–3	4–18	35–99	Quantity of sunlight, was a key variable. Measurements made directly above PC surface	Kim et al. (2018) [138]
Artworks Elephant, London, United Kingdom	TiO_2 painted on walls in a courtyard	Negligible	-	-	-	Seasonal variation and changes in traffic complicated the analysis	Tremper and Green (2016) [139]
A1 and A28 motorways, Netherlands	PC coating added to noise barrier on A1 and porous air quality barrier on A28	Negligible	-	-	-	Negligible performance attributed to short contact times and unfavourable meteorology, including high RH and low T	Dutch Air Quality Innovation Programme (2010) [140]
Guerville (near Paris), France	Model street canyons built at a 1:5 scale, reference canyon compared to canyon with walls clad in TiO_2 mortar panels, artificial pollution source applied	36.7–82.0% NOx	0.1–4.8	-	-	Conclude that variation is due to differences in wall orientation, wind direction and source emissions. Unrealistic SA/V ratio of around 1 m^{-1} is used.	Maggos et al. (2008) [141]
Gaudalupe MRT station, Manila, Philipines	6000 m^2 of wall coated in PC paint, NOx measured at 18 sites with Ogawa passive samplers. Enclosed car park also coated with 9000 m^2 of paint	Outdoor: 10% NO_2, indoor: −51% NO_2	Outdoor: 2.4, indoor: 0.34	-	Outdoor: 82, indoor: 48	Questionable method of RE quantification. UV irradiance far lower indoor than outdoor	Borlaza (2012) [137]
Sir John Cass School, London, United Kingdom	Courtyard wall coated with TiO_2 paint, measurement at 2.5 m	Negligible	-	-	-	Measurement length was not optimal, meteorology may have impacted results	Barratt et al. (2007) [142]

WS = Wind-speed [m s^{-1}], T = Temperature [°C], RH = Relative humidity [%]

Paris

In the model street canyon study conducted near Paris by Maggos et al. (2008) [141], as part of the EU PICADA project, significant NOx removal of 36.7–82.0% is reported for a model street canyon coated with 3% TiO_2 mortar panels from the Italcementi Group, compared with a reference canyon. The methodology appears sound, with a comprehensive suite of pollutants (NO, NOx, SO_2, CO, CO_2, as well as VOCs) and meteorological parameters (WS, T, RH, WD and solar irradiation) measured. However, the study draws criticism for using a SA/V ratio that is an order of magnitude higher than actual street canyons, meaning that the calculated RE should also be scaled accordingly [23,70]. NO was also artificially supplied to the canyon, not a mix of NO and NO_2, NO is removed more effectively than NO_2 by PC surfaces. NOx concentrations were also measured next to the left and right walls of the model canyon (exact distance not given), measurements made closer to PC surfaces are expected to give greater abatement results.

Sir John Cass School, London

In the 2007 study by Barratt et al. [142] an eastern wall of the school was coated with PC paint. The ambient NOx levels 2.5 m from the wall were monitored for 6 months prior to application and for 9 months once applied. The study found that concentrations of NOx dropped after application, but less than other control areas also being monitored, meaning that the paint had at best a negligible impact on air quality. In this case measurements were made at a 2.5 m distance from the wall, measurement closer to the wall may have yielded better results, but would only be relevant if that is where the population typically uses the space.

Artworks Elephant, London

The study conducted at the Artworks Elephant creative hub in London, analysed by Tremper and Green (2016) [139], was designed to improve on previous field studies of PC paint that did not show compelling results for NOx removal, Barratt et al. (2012) [143] and Gallus et al. (2015) [66] (tunnel study). In the study NOx concentrations were measured before and after paint application in a courtyard for 15 months, 9 months pre- and 6 months post-application. A larger surface than in the Barratt et al. [143] study was covered with PC paint and an area with greater average NOx concentration was chosen, to make the abatement by the surface more visible in the analysis. However, measurable NOx abatement could not be detected [139].

Netherlands, Motorway Study

The 2010 report from the Dutch Air Quality Innovation Programme (IPL) [140] aims to identify the best methods for improving air quality and meeting EU standards for PM and NOx along roadways, it is not a peer-reveiwed study but does describe large-scale practical trials conducted by the IPL. It features 6 different potential methods for pollution mitigation along roadways, including adding TiO_2 coated panels to existing noise barriers along a roadway and a subsequent trial with a porous barrier designed specifically for air pollution abatement. No evidence of a resulting improvement to air quality was noted, the report does not describe the analysis conducted but suggests that short contact times and unfavourable meteorology were responsible for the poor results.

Gyeongbu Expressway, Korea

The Gyeongbu expressway study conducted by Kim et al. (2018) [138], describes a study with a similar setup to the IPL report [140], where TiO_2 paint is added to the retaining wall along an expressway. The NOx abatement induced by the PC surface is calculated by comparing the painted section with an unpainted control area. The study reports a NOx RE of 13%. However, this number only takes into account the part of the day when the surface will be most active (between 12:00 and 15:00 p.m.). It is not stated in the study how far from the PC surface the measurements were recorded but from the image shown in the study the sampling line seems to be resting on top of the wall, this would be expected to show a much greater abatement effect than a measurement 3 m away, as recommended for urban air quality monitoring [70,144].

Gaudalupe Station, Manila

In 2013 Borlaza conducted a study of the efficiency of 7.5% TiO_2 paint, this was published in her Master's thesis [137]. This study is referenced in the EIC report [12] and so is discussed here.

Two areas were painted and investigated as part of the study, (1) 6200 m^2 of walls surrounding a busy highway next to the station, and (2) 9000 m^2 inside the basement parking area. The study relies on Ogawa passive samplers for the NO_2 mass concentration reduction analysis, instead of real-time NOx monitors, which are used to compare chronological 'Baseline', 'Activation' and 'Effect' periods for the roadside and in-station sites. Statistical analysis was then conducted on the results from the passive samplers to calculate a possible reduction in mass concentration between the Baseline (December–February) and Effect (July–October) periods.

The study reports NO_2 abatement of 3–25% outdoors, depending on the specific area (average 10%), and a 51% increase in NO_2 for the indoor environment after PC paint application. It is not clear how changes in NO_2 concentration, due to differing traffic and meteorology between the periods, are accounted for in the study. The fact that a 51% increase was observed in the indoor study makes the method seem suspect and the author writes that a cause for the increase in this section may be that the Effect period for the indoor environment included national holidays where significantly more people visit the car park, and that this is the most likely cause of increasing NO_2 during the period. According to this reasoning the fall in NO_2 during the Effect period outdoors may conversely be due to a drop in traffic, increase in wind-speed, or other change in the environment.

Walls Summary

In summary, field studies on the use of PC paint on vertical walls typically report negligible removal, except for studies that use unrealistic conditions or questionable study design. This may be due to their not being enough available surface for PC application, as well as the fact that vertical faces will receive less sunlight over the course of 24 h than a street surface due to the angles and shadows involved [24]. In Colvile et al. (2007) [145], the potential impact of the Barratt et al. (2007) [142] study is modelled and it is concluded that the NOx abatement from coating a single building with PC material would be limited to a very thin layer of the air close to the building surface.

2.2.3. Tunnels and Enclosed Spaces

Semi-enclosed environments such as tunnels give the potential for testing under more controlled environments than, for instance, street canyons. The tunnel environment can be seen as similar to a single-pass reactor, physical conditions are less changeable and a steady source of light can be supplied to the PC artificially, this means it is possible to obtain field test results with less uncertainty.

These factors also mean that tunnels in particular, which have a large SA/V ratio, may be the best candidates for the use of PC surfaces. As artificial light is supplied consistently removal does not rely on favourable meteorology and can operate into the night, meaning the surfaces should be more effective. However, enclosed environments also have drawbacks, including the potential for rapid particle and VOC buildup which can obscure the PC surface. At street level rainwater also serves to wash off nitrates that can build up at the PC surface whereas this will not occur on tunnel roofs [36]. Artificial lighting also adds cost and energy demands relative to outdoor use. The results from the available studies reflect this mix of competing factors, with reported REs of >50% compared with negligible RE, below 2%, as shown in Table 6 and with details below.

Table 6. Tunnels and enclosed spaces.

Location	Test Setup/Metric	Test area dimensions	Light	Removal	WS	RH	SA/V Ratio	Ref
Umberto Tunnel, Rome	Whole tunnel (9000 m^2) painted, 4 NOx analysers in tunnel, compared to monitoring stations in the city	l = 348 m, w = 17 m, h = 8.5 m	UV and visible: 20 W m^{-2}, UV: 2 mW cm^{-2}	23% NOx, 'real' effect $> 50\%$	0.38	40–70	0.23 m^{-1}	Guerrini (2012) [146]
Leopold II Tunnel, Brussels	NOx removal normalised with NOx:CO_2 ratio, comparison of measurements before and after application, up and down wind of active section and in active section with UV on and off	2.5 km long city tunnel, Test section: l = 160 m, w = 8.4 m, h = 4.2 m	UV-A: 1.6 W m^{-2}	<2% NOx	3	70–90	0.4 m^{-1}	Gallus et al. (2015) [66]
Koningstunnel, Hague, Netherlands	650 m long tunnel, KNOxOUT paint added to walls and ceiling, chemiluminescent monitors at the beginning and end of active section, as well as nitrate accumulation strips	150 m test Section	UV: 1 W m^{-2} (wall) and 0.6 W m^{-2} (ceiling)	'significant' NO removal, at around 20%, 'inconsistent' NO_2 results	0.01–3.5	-	-	Kerrod and McIntyre (2004) [147]
Car park	322 m^2 ceiling covered with TiO_2 paint and car exhaust connected to a sealed section of the car park, photocatalytic rates recorded in μg m^{-2} s^{-1}	917 m^3 closed area	Total UV: 1 Wm^{-2}	0.09–0.16 μg m^{-2} s^{-1} NO_2 removal	-	'unstable'	0.35 m^{-1}	Maggos et al. (2007) [73]

WS = Wind speed (m s^{-1}); T = Temperature (°C); RH = Relative humidity (%); l = length; w = width; h = height

Umberto I Tunnel

The study of PC effectiveness for NOx removal in the 'Umberto I' Tunnel, Rome, written by G. Guerrini (2012) [146], contains a lab component conducted by a third party using a recirculation testing method (not ISO standard) and two field campaigns, each three weeks long. TX-Active paint from the Italcementi Group was used and the results are also summarised in a report for the Italcementi Group (2008) [148]. Measurements of NOx, traffic volumes, irradiance, wind speed and other meteorological parameters (RH,T,P) were conducted on weekdays from 8:00 to 16:00. NOx concentrations are measured at the tunnel entrances (or just outside) and in the centre of the tunnel, at 1 m from the surface. To judge RE the study compares measurements from within the tunnel, to measurements from official monitoring stations elsewhere in the city, this is done before and after renovation. RE of 20% for NOx is recorded for the tunnel measurements after renovation, whereas a theoretical RE of >50% is recorded relative to the increase in concentration recorded for the reference sites in the city over the time period. Peaks in pollution concentrations were also dampened, according to analysis of the variance in concentration in the tunnel centre.

Tunnel concentrations after renovation (September–October) are compared to the tunnel concentrations before renovation (July), and with reference stations that are kilometres away. It is noted in the study that NOx measurements are strongly influenced by local traffic, including tourist busses that park next to one of the tunnel entrances in spring and summer. This suggests that measurements comparing different seasons and comparison with reference sites of a different nature to the active site may give uncertain results. The study does not compare measurements in the tunnel before and after an area with a PC surface, or with the lights off and on, which may have clarified the efficiency of the PC surface. Due to the prevailing conditions (traffic flow and elevation) the prevailing wind direction in the tunnel is from one end (via Nazionale entrance) to the other (via del Tritone entrance). Meaning that the NOx concentrations measured at the Nazionale entrance have not passed through the tunnel containing the PC paint, the average concentration and variance in NOx also decrease for the Nazionale entrance measurements, as well as the tunnel centre measurements, when comparing the two periods.

Leopold II Tunnel

The construction of the test site in the Leopold II Tunnel is described in Boonen et al. (2015) [89], and the analysis, conducted by Gallus et al. (2015), is detailed in [66]. This study uses a number of metrics to quantify the RE of the PC surface, including NOx monitoring before and after application of the material, as well as concurrent monitoring upwind and downwind of the active PC tunnel section, and downwind monitoring with and without the UV lights switched on. Pollutant levels were also normalised relative to the photocatalytically inert carbon dioxide emitted by the vehicles. Lab studies were also conducted, according to the ISO standard [49], to investigate potential deactivation of the surfaces, these are detailed in [89]. Photocatalytic paints from the same company as in the Umberto I Tunnel study are used in this study (Italcementi Group, TX-Active and TX-boosted). The results from the study are jarringly different however, with no significant impact on NOx levels recorded and RE <2%. This poor performance is partly attributed to high WS, moderate UV and high RH, but also to deactivation of the PC surface, demonstrated in the lab studies, and potentially caused by VOCs and soot obscuring the PCO surface.

In the study, upper limit calculations for possible RE in this environment are made, using uptake coefficients from the laboratory tests and treating the tunnel as a flow reactor, described in Section 2.3. Under the actual conditions of testing, an upper limit of 0.4% NO RE was calculated, while under under optimum conditions, e.g., greater UV irradiance, lower WS and lower RH, a theoretical RE of 20% was calculated, for NO removal, if no deactivation were to take place.

Koningstunnel

This is not a peer-reviewed study, rather a technical report produced by CRISTAL [147]. The study seems to be conducted in a standard format, with measurements of NOx before and after an active test area, as well as RH, T, WS and frequency of cars through the tunnel. The ceiling and walls of the test section were painted with active TiO_2 paint and lit with UV lamps. Laboratory tests ('similar' to ISO standard) demonstrated that the surfaces could reduce NO_2 levels by up to 50% under lab conditions, with the same UV irradiance as was provided to the tunnel ceiling. In the field the study found NO removal of around 20% but only 'inconsistent' NO_2 removal. They conclude that it is difficult to measure an impact from the PC material when initial NOx levels are low.

Car Park Studies

A car park was artificially closed in order to test PC paints at scale, using actual car exhaust gasses, by Maggos et al. (2007) [73]. RE was not calculated in the form it would be for a flow-reactor and therefore the results of the study are difficult to compare to others. Instead photocatalytic rates in $\mu g\ m^{-2}\ s^{-1}$ are calculated. Overall the results showed that models based on lab results over-estimated the efficiency of the actual tests, which may be due to inhibition of the surface by VOCs, which were present in the car park but not the laboratory testing. In the Thesis by Borlaza [137] (details in Table 5) indoor tests inside a car park are also performed, however an increase in NO_2 concentration of 51% was recorded. This may be due to, low light level ($0.025\ W\ m^{-2}$), very low humidity and problems with the testing method, described in Section 2.2.2 [137].

Tunnels and Enclosed Spaces Summary

The car park studies are not directly comparable to other studies due to differences in the test setups and/or performance metrics used. Conversely, the tunnel studies are directly comparable, yet give vastly different results, from negligible removal up to >50%. Of the two peer reviewed tunnel studies, The Leopold tunnel study [66] has a more rigorous testing regime, using repeat tests, multiple metrics for RE in the tunnel, which are also normalised against CO_2, as well as ISO standard laboratory tests. Whereas, there are potential issues with the experimental design in the Umberto tunnel study, such as having active and control scenarios that are not directly comparable. However, in the Leopold study it is calculated that in an 'ideal' situation where, for instance, there is no surface deactivation and physical parameters are consistently favourable (low RH, low WS, high UV) a 20% RE, similar to the lower estimates for the Umberto tunnel, could be achieved (although only for NO). Meaning that the results may not be contradictory. Overall these field studies illustrate that PCO may be a viable option in very specific cases, but that site-specific testing, with comparable active and control cases, is paramount. It should be noted that, apart from pollutant build-up, the tunnel example represents near ideal conditions for PC activity with far higher SA/V ratios than in a street canyon and with powered UV lights, although installation and maintenance costs are also greater. Therefore, high REs from tunnel studies can not be used to justify the application of PC materials to outdoor walls and street canyons. The Leopold II study also raises questions over the longevity of PC surfaces in harsh/polluted environments.

2.3. Modelling

A small number of relevant modelling studies have been identified, they are described below. There is not a general consensus from the models produced so far, this reflects the range of results seen in the field studies.

In the 2016 AQEG report [24], a model simulation is produced using the ADMS-Urban model 5.0, in the report it is stressed that the model results are highly uncertain due to the complexity of deposition processes in urban environments, but also that NOx deposition fluxes will be an order of magnitude smaller than the emission flux and so it is not possible for PC surfaces to have more than a small impact on NOx concentrations. With this model applied to the painting of an individual street canyon with PC paint, or 'London-wide' PC paint application, NOx abatement is up to 0.7%.

In the EIC report [12], a model is also developed for both road and wall PC coatings in a street canyon. The model predicts 4.4–11.0% NO_2 RE depending on the season and level of coverage, and uses deposition rates an order of magnitude greater than in the AQEG model, it notes that these values are comparable to studies in Rome [146] and Manila [137], these are discussed in Section 3.8. The study claims that it gives a conservative estimate for NOx abatement, but the model does not include changes in RH, light levels, temporary loss of performance due to nitrate build-up, permanent loss of performance due to wearing, or production of byproducts. Presumably including these would substantially lower the modelled results, particularly in winter months [78,131].

In Dylla et al. (2013) [149], a model is created for removal of NO by an asphalt road surface, spray coated with TiO_2, using statistical data from a field study and kinetic data from a lab study of the same surface with a Langmuir–Hinshelwood model. RE percentages are not calculated but the results of the lab study show that RH and light intensity have significant impacts on uptake of NO.

A recent modelling study from Jiang and Yu (2020) [150], modelled NOx abatement of doped TiO_2 surfaces applied to roadways. It calculates 30–80% NO_2 removal on the road and 3–30% on the pavement, using doped TiO_2. It uses NO_2 concentrations of 6000 ppb on the road and 2500 ppb 25 metres from the road, which are massively elevated relative to an urban environment in the EU. In the model there is greater relative removal at higher concentrations. For the solar radiation, 50 W m^{-2} of UV light, corresponding to a clear day at the tropic of cancer, is used, the reaction rate from a lab study of pure TiO_2 was used but multiplied by 5 to account for doping and a further 5 times to account for the fact that 10 W m^{-2} was used when obtaining the rate [67]. Relative humidity and short or long term wear are not mentioned. The results of this model appear to be an upper limit for removal under idealised conditions.

The 2015 tunnel field study conducted by Gallus et al. [66] also contains a lab component and simple model calculations to determine the upper limit for NOx abatement in a tunnel, using values for uptake from their own laboratory experiments. They also develop a general tunnel model tool, that can used to calculate the upper limit for other tunnels, with inputs for WS, SA/V, length, RH and UV irradiance. Their model calculations yielded an upper limit of 0.4% NOx RE for the conditions in the Leopold II tunnel, which corresponds with the $<$2% RE recorded in the field study. If optimum conditions in terms of UV irradiance, WS and RH are used as inputs to the model (and any passivation is ignored) then RE increases to 20%, this illustrates how models that do not take into account these factors may be over-estimating RE relative to real-world conditions.

In Lira et al. (2019) [151], a 2D CFD model was created using ANSYS CFD (Fluent) version 14, and validated against literature data from Ballari et al. (2010) [152]. The model considered changes in RH, light intensity and inlet NO concentration. REs of 12% NO and 16% NO_2 were calculated, respectively.

Moussiopoulos et al. produced a model for the effectiveness of PC paint in street canyons as part of the PICADA project (2008) [153]. The numerical model MIMO, a 3D RANS CFD code for simulating wind-flow in urban areas was used. Source removal rate was taken from a field campaign using a model street canyon conducted by Maggos et al. [141], described in Section 2.2.2. The model indicated a 50–60% NOx RE from the PC surfaces, this was in good agreement with the field results, however the field study has been criticised for having a SA/V ratio that is an order of magnitude greater than an actual street canyon [23].

Modelling Summary

As mentioned above the modelling studies have a broad range of results, from 0.4 to 80% removal for similar cases. This stems from the range of results in field studies and range of modelling approaches. There is not evidence of any model for RE that takes into account seasonal changes in RH, rainfall and solar radiation, as well as de-activation (short or long term), which have been shown to be key parameters in a number of field studies. It is highlighted in Monks et al. (2016) [24], that models of NOx abatement are inherently uncertain due to the uncertainties of the inputs, chiefly the complexity of modelling the atmospheres interaction with surfaces in urban environments. There seems to be disagreement in different models over whether meaningful removal is even possible due to mass transport issues.

3. Discussion

3.1. Impact of Physical Parameters

As described in Staub de Melo and Trichês (2013) [59], based on the available laboratory studies, there is a general consensus around the impact of physical conditions, in particular, humidity, flow/wind speed, initial concentration, and levels of irradiation, all have significant impacts on the efficiency of PCO surfaces [59]. Increasing irradiance levels improves performance, whilst increasing flow rate will lower it [57,58,69,71].

A slight deviation from the general consensus occurs with RH, where some studies found a more complex relation. Lowering RH below a certain level (10%) was found to adversely affect RE, but above this level increasing RH lowered the RE of the surface [34,71]. This is attributed to competition for adsorption sites between water and NOx at higher concentrations, as well as the fact that water is needed for the creation of hydroxyl radicals, a reactant in the trapping of NOx, and so at very low humidity a lack of RH can also be limiting. The exact level of humidity where it changes from promoting to inhibiting NOx removal seems to be related to the PC material surface and other environmental conditions [71].

The impact of RH seems to be a key factor in performance, as described in a number of lab studies performance drops significantly in the range of 70–80% RH [22,57,58]. In Europe for example, 12-month average RH was between 74 and 78% in the years 1980–2016 [154], meaning that performance would be considerably impaired relative to lab testing at 50% RH.

It is also shown in Jiménez-Relinque et al. (2019) [78], that the hygroscopicity of the substrate material, and hence its hygrometric inertia, is what will determine the humidity of the surface. The current measured humidity of the air is different from the substrate humidity which will depend on mean humidity over the preceding days. The number of days that should be considered will depend on the specific hygroscopicity of the substrate [78]. Although, it is also shown in other studies that NOx removal by the surface will be negligible whilst it is raining, or the surfaces are covered in dew [69].

While it has been shown in lab studies that increasing inlet concentration of NO will lower PC performance, in terms of relative removal (RE), lab tests are generally conducted at elevated concentrations, e.g., 1000 ppb. Whereas in the ambient environment concentrations are typically in the low ppb range, for instance monthly mean NOx in London, which is considered to have relatively high pollution levels for Europe, did not exceed 200 ppb in the years 1993–2003 [155]. Testing at this elevated concentration may negatively misrepresent performance for ambient use. In Laufs et al. (2010) [23] PC paints were shown to have first-order kinetics, with removal independent of inlet NOx concentration in the range 25–950 ppb.

Irradiance, particularly in the UV region has been shown to impact RE. This will also differ depending on where the PC surfaces are installed, due to local characteristics of the site, such as surrounding building heights, degree of shadow coverage, and more generally, latitude from the equator. It is noted in the 2016 review by Mcaphee and Folli [38], that UV light is typically quoted as 3–5% of total solar radiation, but this is only the case at solar noon for latitudes below 35°, which discounts Europe, half of Asia and the majority of the United States. This analysis is based on a 2014 study by Folli et al. [131] which is devoted to modelling at which latitudes and during which seasons it is possible for TiO_2 based photocatalysts to remove NO effectively. In the study, modelled irradiance is compared with measured NO removal by a PC surface located in Copenhagen, Denmark (55.68° N) from 2012 to 2013. The results show that the surface only measurably lowered NO concentrations when UV% was $>2.5\%$, and that this was only the case for 6 months of the year. This demonstrates that latitude and the corresponding UV% is a key consideration for PC sites, as in this case annual RE would be at most half of that measured in mid-summer.

Overall it is clear that environmental parameters, particularly irradiance and RH are key to performance. If these are not properly accounted for in models and when reporting results from short term field studies, then significant over-estimations of performance may result.

3.2. Durability

Degradation in performance of TiO_2 has been identified as a significant issue by a number of field and lab studies. Both in the form of temporary loss of performance due to nitrate build-up, which occurs rapidly (days), but can at least partially be washed away, and longer term loss of performance (months) due to, abrasive wear, poisoning of the surface, weathering, carbonation and other permanent mechanisms.

The rate of decay in performance in a specific case will depend on the prevailing conditions as well as the individual active and support surfaces and method of incorporation.

It appears that TiO_2 cast into the bulk of concrete, or in cement slurry coatings, will last longer than sprays of TiO_2 suspension/emulsion on to concrete for areas where abrasive wear is expected [76–78,84], although this will increase the cost of retro-fitting the technology onto existing roadways. The physical and chemical properties of concrete itself also appear to contribute to increased durability over asphalt and glass substrates [82]. Conversely, in another study asphalt coated surfaces had superior durability to concrete [77].

There is also the issue of temporary loss of selectivity and activity due to build up of nitrates on the surface, as well as other species from the ambient environment. This loss can at-least partially be regained by washing the materials [21,89,156]. In some studies it is claimed that periodic rainfall is sufficient to remove these nitrates entirely, but in studies where samples were removed from the field and manually washed, RE was significantly improved, demonstrating that rainfall alone is not sufficient to maintain high efficiency [76,85]. In the tunnel study conducted by Boonen et al. (2015) [89], rinsing with water as well as high UV and a flow of clean air was necessary to restore activity after field exposure. In Staub de Melo et al. it is noted that neither rainwater or standard cleaning is sufficient for re-activating PC blocks and that high-power jets are necessary [76].

Paradoxically, low moisture is required for effective PC removal, but water is also necessary to maintain efficiency. This is studied in detail by Patzsch et al. (2017) [21], who conclude that the NO_3^- oxidation product is not merely blocking active sites but poisons the catalyst and lowers both selectivity and activity. They suggest that the frequency of rainfall at a proposed installation site should be considered when testing a material so that tests can be performed with surface nitrate levels that better represent the materials use in the ambient environment.

Overall, durability depends on a large number of factors, related to both the material and installation site, and is therefore difficult to model, but is key to the assessing the viability of PC surfaces. From the results so far, spray-coating TiO_2 suspensions/emulsions onto existing roadways does not seem a viable option in terms of durability [69,77,84], neither does the use of TiO_2 paint in highly polluted areas [89].

Overall it appears that the issue of durability has been overlooked in many publications [12]. This seems a glaring oversight when performance has been seen to, for example, drop by 50% after 2.5 months [77], be lost entirely after 2.5 months and 11 months [69], and lose 87% RE within a year [76]. Inclusion of accurate rates for loss in activity would have a large effect on future models and cost-benefit analyses, and more research should be conducted into this in the field [24].

3.3. Selectivity

Another overriding issue when reviewing both lab and field studies is that, even if the same type of metric is used, for instance RE or μg m^{-2} s^{-1} of removal, it may be calculated for NO removal only (counting conversion to NO_2 as removal of NO), NOx removal, or NO_2 removal, which will yield significantly different results for the same material, depending on its selectivity. As NO_2 is considered far more harmful, and difficult to remove with PCO than NO, the NO_2 removal, or at least NOx removal are more relevant metrics. However, in most lab studies (including those conforming to the ISO standard) only NO is supplied as a pollutant and so NO_2 RE can only be negative or zero, whereas calculating NOx removal will ignore conversion of NO to NO_2 [144].

In many studies this conversion is entirely overlooked, but it has been shown that use of unmodified TiO_2, for instance the reference material P25 (Evonik Degussa), will typically result in net production of NO_2 when NO is introduced to the surface [71,157], and this is consistent with a large number of other TiO_2 studies, particularly for rutile TiO_2 [22,34,116,152,158–165]. This is also confirmed by field studies, for instance in Folli. et al. (2015) [56], where overall NOx abatement was up to 30%, but changes in NO_2 concentration were negligible, similar results were also seen in the field by Fan et al. (2018) [84] and Kerrod et al. (2014) [147].

An alternative metric, the 'DeNOx index' is introduced in Bloh et al. (2014) [157]. This aims to combine measurement of selectivity and activity into a single number by assigning toxicity values to both NO and NO_2 and then indicating total change in toxicity. In the DeNOx index, NO is arbitrarily assigned a relative toxicity value of 1, and NO_2 a value of 3, based on direct and indirect health impacts, meaning that the selectivity threshold for a positive index is 66.7%. In Bloh et al. [157], a number of reference and newly synthesised TiO_2 samples are tested for NO abatement and their DeNOx index is calculated. All of the reference materials had a selectivity of 30% or less, meaning an unfavourable DeNOx index and negative net effect on air quality, according to this metric, under the conditions used. Similarly, in the review of photocatalytic concrete made by Macphee and Folli (2016) [38], it is concluded that conventional TiO_2 is not selective enough and often has a large negative DeNOx index, meaning that more fundamental research is needed before it can be deployed successfully.

The DeNOX index could represent a step forward in the accurate ranking and comparison of PC materials but has not yet had a large uptake. It may also penalise materials tested under ISO standard conditions, where pure NO is used as the inlet pollutant, instead of a NO:NO_2 mix, as there is no potential for NO_2 removal, only NO_2 production. In order to use this index as standard, and to make testing more relevant to ambient conditions, a new testing method should be designed and accepted. Assigning an accurate toxicity index to the two pollutants is also not trivial. NO_2 is considered far more toxic than NO, for instance, threshold limits for nitrogen oxides in ambient air, published by the EU [7] and WHO [5], are specifically for NO_2 only. In terms of workplace limits the NO threshold is 25 ppm, whereas the NO_2 threshold varies between 1 and 3 ppm, or 8–25 times lower than for NO [166].

Although there is not a direct health benefit from reduction of NO in street and urban environments, in the ambient environment there are indirect health benefits associated with converting it to nitrate, due to the atmospheric chemistry of NO. NO_2 is rapidly formed from NO through its reaction with O_3. At night time, under typical urban conditions, NO will be transformed in to NO_2 until either all the NO is converted to NO_2, or until all the O_3 is consumed (O_3 limited conditions). Given typical concentrations in the urban atmosphere this reaction takes place on a time scale of just a few minutes, but this is dependent on concentrations and temperature. In addition to the conversion of NO to NO_2 the major daytime reaction that affects NO_2 is destruction by photolysis, i.e., sunlight breaking down the NO_2 molecule into an NO molecule and a ground state oxygen molecule. This reaction rate may also be quite fast (10–30 min) in sunny environments. As a result, a balanced 'photochemical steady state' can be reached within an hour, such that the production of NO_2 is balanced by its destruction.

In urban and street environments with relatively low NO levels, like in Denmark, reductions in NO by PCO surfaces, that are active during daytime, will most likely lead to lower NO_2 levels (as long as they are selective to nitrate). During many hours there will be enough O_3 present to oxidize NO to NO_2, as O_3 is not the limiting factor for formation of NO_2 as it was decades ago when NO levels were much higher. In street environments with relatively high NO levels, O_3 will still be limiting factor for formation of NO_2, and hence reductions in NO will not lead to reductions in NO_2. Although, VOCs can also interact with the PC surface and be degraded to formaldehyde and acetaldehyde, which are ozone precursors and feed into the smog cycle, further exacerbating and complicating the issue [31–34].

Further, even if NO is not oxidized to NO_2 in the street environment, lowering NO will result in less formation of secondary particles in the atmosphere (less nitrate) and reduce the health burden of $PM_{2.5}$. However, this will take place far from the application of photocatalytic materials as the transformation from NO to nitrate is slow in the atmosphere.

Due to the rapid inter-conversion of NOx species, the effect of PCO surfaces on NO and NO_2 photochemical steady state concentrations is a complex issue. It appears that more work is needed to establish an accurate metric for the net effect of PC materials, as well as a standardised testing regime that mimics ambient conditions. It seems clear however that when conventional TiO_2 is used for photocatalysis there will likely be an overall negative effect on air quality and doped, or otherwise modified TiO_2 products, are necessary.

3.4. Material Improvements

Table 3 display the burgeoning recent research into improvement of PC surfaces. Although improvements to activity are welcome, as can be seen from Section 3.3 above, improvements to the selectivity of PC surfaces is the key to making them viable. Improvements have been achieved in the lab environment via alterations to the support material, in particular with alkaline concretes [96,112], and by doping the TiO_2, for instance with Wb and N [38], although selectivity improvements can come at the cost of activity loss [38]. There have also been impressive results recorded for doping with noble metals Au, Pt and Pd [104,107,121], yet their inclusion may add significantly to the overall cost of PC surfaces.

In terms of doped TiO_2, large-scale field studies have only been recorded for carbon-doped TiO_2, as described in Section 2.1.3, with mixed results. Further, standardised, field testing is needed to prove the efficacy of doped-TiO_2 in the field. Depending on the results of these field tests and the costs of doped materials developed so far, further development is most likely necessary [38].

3.5. Comparison of Field Studies

As described in Section 2.2, there is great variability in the results for NOx abatement in all categories of field study, from ≤ 2 to 66% in street studies, negligible to 82% for wall studies, and for tunnels and enclosed spaces, negligible up to 23%, with a calculated 'real' effect of $>50\%$ (as well as -51% for an indoor car park). This range of results is partly due to differences in the TiO_2 surface itself, for instance doped or un-doped and concrete compared with paint or asphalt, as well as differences in key external parameters at the location such as WS, RH, irradiance and pollution level. However, it seems that a large degree of the variation reported in efficiency is also due to differences in the study design and metrics used to quantify NOx abatement.

As described in Section 3.3, the metric used will alter the results, depending on a materials selectivity:activity relationship. It is also crucially important whether a reported RE is averaged over a short 'measurement period', 'day time' (which can presumably be defined as between 8 and 16 h), or averaged over a full 24 h per day. This means that 20% reported RE can instantly be cut to 10% if recorded for day time only, or cut even further if this is recorded during a short period of higher irradiance, as is the case in Kim et al. (2018) [138], where RE is recorded between 12:00 and 15:00 p.m. As noted in the study by Gallus et al. (2015) [70], in order to comply with the EU regulations for lowering average annual NO_2 concentrations below 40 µg m^{-3} (Directive 2008/50/EC [7]), 24 h averages should be used (and ideally with measurements made in all seasons, as shown in Section 3.1). If the purpose is to smooth periodic spikes in NO_2 (200 µg m^{-3} as a 1 h average should not be exceeded more than 18 times per year in the EU [7]), shorter averages may be useful, however the averaging time should be quoted with the RE for clarity, and again should be averaged from measurements across all seasons. This is only one of the parameters that differs between studies but can mean the difference between a 'successful' or 'unsuccessful' field study.

There are other key elements of field studies that are not standardised. For instance, the study design can also greatly alter the reported RE. In some studies, such as Maggos et al. 2008 [141], impressive REs of between 40 and 80% are reported. However, as noted in Laufs et al. (2010) [23], SA/V ratio is a rate limiting parameter and in a typical street canyon (20 m width) the SA/V is 0.1 m^{-1}, whereas in the artificial street canyons used in Maggos et al. (2008) [141] this ratio is 1 m^{-1}, an order of magnitude greater. Therefore, in order to be relevant to an actual street canyon, the RE in this and other similar studies should be scaled accordingly, bringing the results in line with other, more conservative, studies at ∼5% [23,70]. This is presumably why field studies documented for PC coatings on barriers along motorways/highways reported low or negligible RE, as SA/V is typically lower for these sites and contact times for pollutants at the PC surfaces are also low [132,140,167]. If, as claimed in Laufs et al. (2010) [23], and based on kinetic studies, NOx uptake is limited by transport, then further improvements to PC surface activity will not significantly improve performance.

Another parameter that will alter the recorded RE is the NOx sampling distance from the PC surface, for instance, in Barratt et al. (2007) [142], where measurement was at 2.5 m from a wall, no decrease in NOx was seen during the study. Other studies, reporting greater NOx abatement, measure at a range of distances including, 0.05–1.5 m [69], 0.30–1.8 m [135], 0.5 m [55], 2 m [56], and in other studies measurement height is not mentioned [84,138]. In Gallus et al. (2015) [70] (where negligible removal was recorded), measurements were conducted at a 2.5 m distance and 3 m height, and it is noted that 3 m height is the recommended standard for urban air quality monitoring stations. Change in RE with sampling height is demonstrated in Ballari et al. (2013) [69], where the RE of a PC pavement is recorded at 5, 30 and 150 cm, and RE was increased by 30% and 37% when moving from 150 cm to 30 and 5 cm, respectively. The exact relationship will depend on environment specific parameters but is expected to be significant in all cases.

The available field studies also use a range of methods to quantify the effect of installing PC surfaces. One method is to compare two areas, an active area where PC NOx abatement occurs, and a control area that is unaltered, but design of field tests with effective control areas for comparison to active areas is complex. The same area can be compared before and after PC treatment, or with and without illumination in the case of tunnels, but the ambient NOx levels can also change during this time, due to seasonal changes or other factors such as national holidays occurring during either the control or effect period. It is difficult to separate the relatively small changes in ambient NOx concentration induced by the surfaces from variability in local emission sources or meteorology [139]. Therefore, this approach often leads to inconclusive results or claims that are not robust [137,142].

Tests can also be conducted by bringing a portable testing unit to a field-site that can be placed over the installed PC surfaces, NOx RE can then be calculated from the concentration difference between the inlet and outlet of the reactor, either sunlight or artificial UV light can be used for excitation [36,168]. This is useful for quantifying changes in performance of PC materials in the field over time, determining their durability, but does not compare directly to other field studies which measure the effect of the PC materials on the NOx concentration in surrounding ambient air.

Otherwise, separate active and control sections of a street or streets can be compared concurrently, but in this case there can be issues with differences in sources, meteorology and mixing/dispersion between the areas [24,70]. These spatiotemporal inconsistencies mean neither method is perfect, although concurrent measurement at comparable active and control sections is generally preferable. In some studies, model street canyons were built, meaning the reference and control canyons could be as similar as possible, but so far these have only been built at a fraction of the size of actual street canyons, which again alters the results [23,70]. The different methods used in the different studies contributes to great uncertainty when comparing final results.

Perhaps the study with the most comprehensive quantification is the study conducted in the Leopold II tunnel [66,89], it utilises a range of methods (described in Section 2.2.3), including many of those mentioned above, as well as normalising pollutant levels relative to the CO_2 also produced by traffic, that is inert to PC surfaces. A lab and modelling component is also included. It records RE $<2\%$, although this is concluded as being due to low irradiance levels, high pollutant concentrations and otherwise unfavourable conditions.

Conversely, the study of a photocatalytic street coated in C doped TiO_2 in Hengelo, Netherlands conducted by Ballari et al. (2013) [69], and described in Section 2.2.1 also appears to be comprehensive, including a monitoring period that spans more than a year. It reports a much greater average NOx RE of 19%. There are caveats to this result, only daytime results were recorded for averaging and a range of measurement heights was used (0.05, 0.3 and 1.5 m) and the average RE from all heights is reported, specific NO_2 abatement was not reported. There was also negligible or minimal removal recorded on days where it was rainy, very windy, very humid, when there had been a number of days without rain and nitrates were built up on the surface, and when the coating had decayed. Days where a PC effect was not seen were excluded from the averaging to produce the 19% value. The efficiency of the first material tested was negligible (blocks pre-cast with TiO_2), the second coating, a spray C-TiO_2 suspension, was effective but its efficiency decayed and was negligible after 2.5 months, a second coating was then added that lost its efficiency at a lower rate and but was also found to have negligible removal after 11 months. Therefore, this study could be said to disprove the notion that mass transport limitations mean that PC surfaces can not significantly alter NOx concentrations, due to the significant removal recorded under favourable conditions, however the 19% average appears inflated relative to an average annual RE, under all conditions, at an appropriate distance from the surface and accounting for wear to the surface. In Gallus et al. (2015) [70], it is concluded that the results of previous studies to that date, if averaged diurnally and extrapolated to representative urban conditions, would be in the same range as their own study at $\sim$2%.

3.6. Comparison of Lab Studies

Typically the results from laboratory studies are more homogeneous than the field studies. This is to be expected as more controlled conditions are used, and there are recognised standards. Lab studies also typically yield significantly higher RE performance, with NOx RE in the region of 40%, under standard conditions. This again is expected, due to the conditions used, i.e., only NO as an inlet gas, greater UV light levels, lower flow rates and humidity levels, and testing in the absence of co-pollutants such as VOCs [12,74,75,128,144].

Although the results of laboratory studies are more homogeneous than the field results, there are still issues with standardisation. For instance, there are different laboratory standards used for testing PC removal of NOx [49,51,144], and some studies do not conform to any recognised standard, and/or quote different metrics for NOx abatement. Of all the studies in this review $\sim$50% are undertaken using the ISO standard, so results from these studies are most comparable, studies that use their own unique laboratory setup and metric, without standardisation, are generally not useful in detailing improvements to materials. Within the ISO standard there are also a number of issues. Some of the studies which do not use it do so because the standard conditions are not relevant to actual conditions in the urban environment, in particular NO levels are too high (1 ppm), while NO_2 is not added at the inlet [144]. Chemiluminescence NOx monitors are typically used in the lab studies (and most field studies), the operating principles of these monitors, which only directly measure NO, can not distinguish between NO_2 and other oxidised nitrogen species (NO_y), this means that other reaction products such as HONO will be mis-characterised as NO_2, affecting the calculated RE, and meaning hazardous by-products are not identified [144]. In Ifang et al. (2014) [144], the key issues with current lab testing standards are outlined and a modified method is proposed, that is better standardized and aims to also measure the potential negative impacts of PC surfaces. It recommends the use of NO_2 at concentrations < 100 ppb, adding 'turbulence barriers' to flow-reactor to remove diffusion limitations and that adsorbed nitrate is quantified, among other changes. It also proposes the use of uptake coefficients instead of other metrics that are dependent on experimental conditions.

This type of standard, that contains realistic environmental concentrations and physical conditions, is necessary for more accurate comparison of materials. However, other facets of a field campaign, such as co-pollutants, rainfall, seasonal changes and abrasive wear can not be easily reproduced in the lab and will vary across different field sites. Therefore, site-specific evaluation will still be necessary.

3.7. Modelling Results

As described in Section 2.3 there is a large range in the reported modelling results, reflecting the uncertainty in field tests. Until there is standardised field and lab testing the modelled results will also remain uncertain. However, it should be mentioned that models which do not take into account seasonal changes in humidity, irradiance and rainfall, as well as wear to the surfaces can only represent upper limits of potential RE [78,131].

3.8. Previous Review Efforts

As mentioned in Section 1.4, the most relevant recent reviews are the AQEG [24] and EIC [12] reports. Macphee and Folli also produced an article which reviews the physico-chemical factors affecting cement-based PC (2016) [38]. These are discussed below.

The AQEG report presents a negative overall view of the materials, stating that the more comprehensive field studies (conducted mainly as part of the PhotoPAQ project) do not report a significant reduction in NOx, and they claim that based on modelling studies it is not physically possible for enough air to interact with the surfaces to provide significant removal of NOx, even if the surfaces are highly active. They also highlight the possibility of the release of harmful by-products, such as HONO and HCHO from the PC surfaces. In conclusion they do not recommend further trials, but write that any future trials should robustly quantify changes before and after PC application, investigate performance under a complete mix of potential urban pollutants and further investigate potential deactivation [24]. Evidence from the field studies in this review would dispute the results of the model, as the results of studies with robust testing procedures report significant impacts on NOx concentrations. For instance, Folli et al. (2015) [56] report a maximum NO RE of 45%, demonstrating that a PC street surface can have a significant impact on NO, even if the surface is not selective, and Ballari et al. (2013) [69], one of the most comprehensive field studies, also report significant NOx RE of 45% under optimal conditions. This suggests that NOx abatement is physically possible in terms of air-to-surface interactions.

The EIC review, which includes a report commissioned from Imperial College London [12], was produced 1 year after the AQEG report. It presents a more positive outlook. The report covers a larger range of field studies (12:5), although in this it includes more grey literature that is not peer-reviewed. For instance, reports made by companies producing PC paints [147], and a Master's thesis [137].

They conclude that although the field results present variable success 'it is clear that in other trials, substantial reductions in ambient NOx levels were observed' and references the Manila [137] and Rome [146] studies as evidence for this.

However, it mis-characterises the Manila study claiming that NO_2 concentrations were ‘reduced by up to 23%’ which is technically true but the conclusion states an average removal of 10%, with a range of 3–25%, which the authors of this study consider the appropriate metric. The EIC report also fails to mention that a significant increase in NO_2 of 51% was recorded in the indoor parking garage also measured in the study, and the issues with the study design noted by the author, which are described in Section 2.2.2. The Rome field study [146] mentioned in the IEC report is a tunnel study, the merit of the study is discussed in Section 2.2.3 but overall tunnel study results can not be extrapolated to apply to street canyons or other outdoor areas due to the far higher SA/V ratio in tunnels and the possibility of including an artificial constant UV light source, which also increases installation and maintenance costs.

In the EIC report a model is also produced, it predicts NO_2 RE of 4.3–11%, as described in Section 2.3. This can be viewed as an upper limit due to not taking into account a number of factors which lower RE over the course of a year, and using a high coverage scenario of all the ground surface and half of the buildings in a street canyon, during summer, to reach 11%. Despite the more positive outlook based on the Rome and Manila studies, the authors still recommend further trials in order to assess PCO NOx abatement more conclusively. They also recommend better standardisation in field and lab studies, certification for commercial products, further studies into hazardous by-products and better cost-benefit analyses that consider meteorological conditions.

The 2016 review of photocatalytic concrete conducted by Macphee and Folli [38], focuses chiefly on results from lab studies and not large scale field studies, despite this it strongly highlights that the high activity of conventional TiO_2 combined with low selectivity makes it unsuitable for real-world use, having a negative DeNOx index [38].

Overall the results of this review are in agreement with the conclusions from the previous reviews, barring the model results, and the conclusion of the EIC report that further testing is not recommended. Based on the available evidence, the authors of this study conclude that further field trials of modified TiO_2 surfaces may yet yield compelling results.

4. Conclusions and Summary

The main focus of this review is to assess the available field studies for NOx abatement by PCO surfaces in urban environments. Compelling evidence of significant NOx removal, such as the 20% and above claimed by some studies and commercial reports, was not found, particularly if considering lowering NO_2 below yearly averaged thresholds.

This is an active area of research with many interested parties including PCO material manufacturers, governments and municipalities, and researchers. There is a large range of reported results regarding the efficacy of PCO technology in field studies, with many studies reporting negligible RE for NOx of <2%, but others reporting up to 80%.

The reason for these mixed results seems mainly due to the lack of protocol or standardisation for field studies in the area. The main areas of divergence between studies are: the metric reported, averaging times for removal, the length of the study (e.g., whether multiple seasons are included or not), the SA/V ratio of the experimental site, and the sampling distance from the surface, as well as differences in establishing active vs. control sites, and data analysis. Hence, it seems that under realistic, standardised conditions, the available field studies for PCO use in street canyons can be re-evaluated to present an upper limit of around 4% RE in the daytime and 2% or less if diurnal averages are considered [70,144]. Depending on the study, this RE is only quantified for between 0.3 and 3 m from the surface itself.

There are also legitimate differences in the studies that contribute to the spread in results. For instance, there are a range of active materials on the market, applied to different substrates, that have real differences in efficiency. Doping of the TiO_2 and optimisation of the support material, for instance using C-TiO_2 cast into rough surfaced, porous, alkaline concrete, compared with conventional TiO_2 sprayed onto standard asphalt will significantly affect the results.

It has also been shown in lab and field studies that the physical parameters of, relative humidity, rainfall, irradiance and flow/windspeed have significant effects on RE, meaning that in colder, darker, humid, cloudy climates, or areas with high wind-speeds, PCO materials may not perform meaningful NOx abatement. For instance, in a field study where the PCO concrete was dew covered during the morning rush hour, no NOx removal by the surface was observed [69], similarly the surfaces are not active under mixed high pollutant levels [66], or at northerly latitudes, where UV irradiance is low [131]. Durability is also a problem and it seems that surface performance will decay irreversibly over months and reversibly over days/weeks, this means that re-application and frequent cleaning would be necessary to maintain efficiency under typical conditions [69,76].

Overall, this study agrees with the conclusion that, with all factors considered, there is not compelling evidence for successful NOx abatement by PC surfaces of above ∼2% in urban environments as a yearly average, even under favourable conditions, and that this NOx reduction is typically driven by the removal of NO and not the more harmful NO_2.

There are also other issues with PC materials related to the production of harmful byproducts, such as HONO, VOCs and O_3, meaning that it has the potential for negative air quality impacts if not used correctly [34,169]. The key issue for conventional TiO_2 is that a number of studies have shown it will have an overall negative impact on air quality due to low activity toward NO_2 and un-selective oxidation of NO, leading to increased concentrations of the more toxic NO_2 [22,34,116,152,158–165].

In conclusion, optimised TiO_2 surfaces may be technically viable for use in lowering of NOx levels in specific circumstances, but individual cases should be reviewed and tested to determine if there will be a significant removal of NOx, and particularly, overall removal of NO_2. In most cases the removal (if present) will be far below the RE of 20–80% quoted by some sources, and in fact likely below 2% (for the immediate around the surface), before degradation of the surface occurs. Therefore, in its current state PCO offers at best a small reduction in local NOx concentrations and at its worst a negative overall impact on air quality, without other benefits. Whereas, measures that lower overall emissions of traffic-related pollution will lead to tangible improvements to air quality as well as other co-benefits in terms of environmental and health impacts. Therefore, the effect of PC surface deployment on air quality is highly uncertain, any reductions in NOx will also last for a relatively short time.

However, due to the stream of recent research into continuing improvement of PCO, selectivity, activity and longevity, this situation should be under continual review, but standardised testing in both lab and field environments is also necessary, to confirm the viability of new developments. In future, a durable and selective surface, yielding removal of 2–4% for a cost of ∼€45,000 per ton of NO_2, without other indirect harm to local economy may still be a viable consideration for harm reduction [14,23]. However, this is not yet a reality.

5. Recommendations

In light of the conclusions of this study the following recommendations are made:

- Plain anatase or rutile TiO_2 should not be used as a PCO surface due to their low selectivity and likely negative impacts on air quality. Optimised PCO active components and support materials which are more selective must be developed, or existing improvements from lab studies must be proved in the field.
- A new standard for lab testing, with relevance to ambient conditions, quantification of by-products, and transferable results is necessary.
- A standardised metric is needed for the assessment of NOx abatement efficiency (separating NO and NO_2), which takes into account selectivity as well activity, such as the DeNOx index.
- A standard method for field testing, which accounts for; accurate comparisons of active and control areas, sampling inlet position, averaging times for calculating

abatement, seasonal changes, and durability must be developed to make studies more reliable and comparable.
- Site-specific field testing (as well as lab testing) is necessary before deployment for assessment of performance and passivation. Assessment of the prevailing humidity, rainfall, irradiance and pollution levels at a site should also be conducted before field tests are considered.
- Determination of potential by-products including VOCs and reactive nitrogen oxides is necessary for both the field and lab tests.
- When assessing PCO materials more consideration should be taken for durability in the proposed field environment, abrasive wear, poisoning and nitrate build-up should be accounted for.
- Similarly, modelling should account for loss of performance over time, as well as seasonal changes in weather.
- In future, commercial materials should be tested under standardised conditions and certified for use, to ensure that products which have a negative impact on air quality are not sold.

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Abbreviations

The following abbreviations are used in this manuscript:

AQEG	Air Quality Expert Group
CNT	Carbon NanoTube
EIC	Environmental Industries Commission
I	Irradiance
NOx	reactive Nitrogen Oxides (NO and NO_2)
NOy	all oxidised atmospheric odd-Nitrogen species
PCO	PhotoCatalytic Oxidation
PC	PhotoCatalytic
PhotoPAQ	Photocatalytic remediation Processes on Air Quality
PICADA	Photo-catalytic Innovative Coverings and Applications for De-pollution Assessment
PM	Particulate Matter
Q	Flow
RE	Removal Efficiency
rGO	reduced Graphene Oxide
RH	Relative Humidity
SA/V	Surface Area / Volume (ratio)
SSA	Specific Surface Area
T	Temperature
VOC	Volatile Organic Compound
WD	Wind Direction
WS	Wind Speed

References

1. Nakata, K.; Ochiai, T.; Murakami, T.; Fujishima, A. Photoenergy Conversion with TiO_2 Photocatalysis: New Materials and Recent Applications. *Electrochim. Acta* **2012**, *84*, 103–111. [CrossRef]
2. Byrne, C.; Subramanian, G.; Pillai, S.C. Recent Advances in Photocatalysis for Environmental Applications. *J. Environ. Chem. Eng.* **2018**, *6*, 3531–3555. [CrossRef]
3. Zhao, J.; Yang, X. Photocatalytic Oxidation for Indoor Air Purification: A Literature Review. *Build. Environ.* **2003**, *38*, 645–654. [CrossRef]
4. Cardellicchio, L. Self-Cleaning and Colour-Preserving Efficiency of Photocatalytic Concrete: Case Study of the Jubilee Church in Rome. *Build. Res. Inf.* **2020**, *48*, 160–179. [CrossRef]
5. WHO. *Air Quality Guidelines: Global Update 2005: Particulate Matter, Ozone, Nitrogen Dioxide, and Sulfur Dioxide*; World Health Organization: Geneve, Switzerland, 2006.
6. Directive 1999/30/EC of the European Parliament and the Council. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:31999L0030&from=EN (accessed on 20 May 2021).
7. Directive 2008/50/EC of the European Parliament and the Council. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0050&from=en (accessed on 20 May 2021).
8. London Has Already Reached Air Pollution Limits for 2018. Available online: https://www.newscientist.com/article/2159875-london-has-already-reached-air-pollution-limits-for-2018/ (accessed on 20 May 2021).
9. Zhang, R.; Tie, X.; Bond, D.W. Impacts of Anthropogenic and Natural NOx Sources over the U.S. on Tropospheric Chemistry. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 1505–1509. [CrossRef]
10. Fuentes, J.D.; Lerdau, M.; Atkinson, R.; Baldocchi, D.; Bottenheim, J.W.; Ciccioli, P.; Lamb, B.; Geron, C.; Gu, L.; Guenther, A. Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review. *Bull. Am. Meteorol. Soc.* **2000**, *81*, 1537–1576. [CrossRef]
11. Galloway, J.N.; Aber, J.D.; Erisman, J.W.; Seitzinger, S.P.; Howarth, R.W.; Cowling, E.B.; Cosby, B.J. The Nitrogen Cascade. *BioScience* **2003**, *53*, 341–356. [CrossRef]
12. Environmental Industries Commission. *Towards Purer Air: A Review of the Latest Evidence of the Effectiveness of Photocatalytic Materials and Treatments in Tackling Local Air Pollution*; Technical Report; EIC: London, UK, 2017.
13. Brandenberger, S.; Kröcher, O.; Tissler, A.; Althoff, R. The State of the Art in Selective Catalytic Reduction of NOx by Ammonia Using Metal-Exchanged Zeolite Catalysts. *Catal. Rev.* **2008**, *50*, 492–531. [CrossRef]
14. Environmental Industries Comission. *A Clear Choice for the UK: Technology Options for Tackling Air Pollution*; Technical Report; EIC: London, UK, 2015.
15. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO_2 Photocatalysis: Mechanisms and Materials. *Chem. Rev.* **2014**, *114*, 9919–9986. [CrossRef]
16. Chen, H.; Nanayakkara, C.E.; Grassian, V.H. Titanium Dioxide Photocatalysis in Atmospheric Chemistry. *Chem. Rev.* **2012**, *112*, 5919–5948. [CrossRef]
17. Nakata, K.; Fujishima, A. TiO_2 Photocatalysis: Design and Applications. *J. Photochem. Photobiol. C Photochem. Rev.* **2012**, *13*, 169–189. [CrossRef]
18. Hanaor, D.A.H.; Sorrell, C.C. Review of the Anatase to Rutile Phase Transformation. *J. Mater. Sci.* **2011**, *46*, 855–874. [CrossRef]
19. Luttrell, T.; Halpegamage, S.; Tao, J.; Kramer, A.; Sutter, E.; Batzill, M. Why Is Anatase a Better Photocatalyst than Rutile?—Model Studies on Epitaxial TiO_2 Films. *Sci. Rep.* **2014**, *4*, 4043. [CrossRef]
20. Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. Morphology of a TiO_2 Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases. *J. Catal.* **2001**, *203*, 82–86. [CrossRef]
21. Patzsch, J.; Folli, A.; Macphee, D.E.; Bloh, J.Z. On the Underlying Mechanisms of the Low Observed Nitrate Selectivity in Photocatalytic NOx Abatement and the Importance of the Oxygen Reduction Reaction. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32678–32686. [CrossRef]
22. Ballari, M.M.; Yu, Q.L.; Brouwers, H.J.H. Experimental Study of the NO and NO_2 Degradation by Photocatalytically Active Concrete. *Catal. Today* **2011**, *161*, 175–180. [CrossRef]
23. Laufs, S.; Burgeth, G.; Duttlinger, W.; Kurtenbach, R.; Maban, M.; Thomas, C.; Wiesen, P.; Kleffmann, J. Conversion of Nitrogen Oxides on Commercial Photocatalytic Dispersion Paints. *Atmos. Environ.* **2010**, *44*, 2341–2349. [CrossRef]
24. Monks, P. *Paints and Surfaces for the Removal of Nitrogen Oxides*; Technical Report; Air Quality Expert Group: London, UK, 2016.
25. Monge, M.E.; D'Anna, B.; George, C. Nitrogen Dioxide Removal and Nitrous Acid Formation on Titanium Oxide Surfaces—An Air Quality Remediation Process? *Phys. Chem. Chem. Phys.* **2010**, *12*, 8991. [CrossRef]
26. Langridge, J.M.; Gustafsson, R.J.; Griffiths, P.T.; Cox, R.A.; Lambert, R.M.; Jones, R.L. Solar Driven Nitrous Acid Formation on Building Material Surfaces Containing Titanium Dioxide: A Concern for Air Quality in Urban Areas? *Atmos. Environ.* **2009**, *43*, 5128–5131. [CrossRef]
27. Ndour, M.; D'Anna, B.; George, C.; Ka, O.; Balkanski, Y.; Kleffmann, J.; Stemmler, K.; Ammann, M. Photoenhanced Uptake of NO_2 on Mineral Dust: Laboratory Experiments and Model Simulations. *Geophys. Res. Lett.* **2008**, *35*. [CrossRef]
28. Monge, M.E.; George, C.; D'Anna, B.; Doussin, J.F.; Jammoul, A.; Wang, J.; Eyglunent, G.; Solignac, G.; Daële, V.; Mellouki, A. Ozone Formation from Illuminated Titanium Dioxide Surfaces. *J. Am. Chem. Soc.* **2010**, *132*, 8234–8235. [CrossRef]

29. Beaumont, S.K.; Gustafsson, R.J.; Lambert, R.M. Heterogeneous Photochemistry Relevant to the Troposphere: H_2O_2 Production during the Photochemical Reduction of NO_2 to HONO on UV-Illuminated TiO_2 Surfaces. *ChemPhysChem* **2009**, *10*, 331–333. [CrossRef]
30. Laboratory, L.B.N. *Evaluation of Titanium Dioxide as a Photocatalyst for Removing Air Pollutants*; Technical Report; California Energy Commission Public Interest Energy Research Program: Sacramento, CA, USA, 2008.
31. Auvinen, J.; Wirtanen, L. The Influence of Photocatalytic Interior Paints on Indoor Air Quality. *Atmos. Environ.* **2008**, *42*, 4101–4112. [CrossRef]
32. Salthammer, T.; Fuhrmann, F. Photocatalytic Surface Reactions on Indoor Wall Paint. *Environ. Sci. Technol.* **2007**, *41*, 6573–6578. [CrossRef]
33. Geiss, O.; Cacho, C.; Barrero-Moreno, J.; Kotzias, D. Photocatalytic Degradation of Organic Paint Constituents-Formation of Carbonyls. *Build. Environ.* **2012**, *48*, 107–112. [CrossRef]
34. Toro, C.; Jobson, B.T.; Haselbach, L.; Shen, S.; Chung, S.H. Photoactive Roadways: Determination of CO, NO and VOC Uptake Coefficients and Photolabile Side Product Yields on TiO_2 Treated Asphalt and Concrete. *Atmos. Environ.* **2016**, *139*, 37–45. [CrossRef]
35. Kebede, M.A.; Scharko, N.K.; Appelt, L.E.; Raff, J.D. Formation of Nitrous Acid during Ammonia Photooxidation on TiO_2 under Atmospherically Relevant Conditions. *J. Phys. Chem. Lett.* **2013**, *4*, 2618–2623. [CrossRef]
36. Boonen, E.; Beeldens, A. Recent Photocatalytic Applications for Air Purification in Belgium. *Coatings* **2014**, *4*, 553–573. [CrossRef]
37. Boonen, E.; Beeldens, A. Photocatalytic Roads: From Lab Tests to Real Scale Applications. *Eur. Transp. Res. Rev.* **2013**, *5*, 79–89. [CrossRef]
38. Macphee, D.E.; Folli, A. Photocatalytic Concretes—The Interface between Photocatalysis and Cement Chemistry. *Cem. Concr. Res.* **2016**, *85*, 48–54. [CrossRef]
39. Folli, A.; Pade, C.; Hansen, T.B.; De Marco, T.; Macphee, D.E. TiO_2 Photocatalysis in Cementitious Systems: Insights into Self-Cleaning and Depollution Chemistry. *Cem. Concr. Res.* **2012**, *42*, 539–548. [CrossRef]
40. Zhong, L.; Haghighat, F. Photocatalytic Air Cleaners and Materials Technologies—Abilities and Limitations. *Build. Environ.* **2015**, *91*, 191–203. [CrossRef]
41. Chen, J.; Poon, C.S. Photocatalytic Construction and Building Materials: From Fundamentals to Applications. *Build. Environ.* **2009**, *44*, 1899–1906. [CrossRef]
42. Fujishima, A.; Zhang, X.; Tryk, D.A. TiO_2 Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515–582. [CrossRef]
43. Fujishima, A.; Zhang, X. Titanium Dioxide Photocatalysis: Present Situation and Future Approaches. *C. R. Chim.* **2006**, *9*, 750–760. [CrossRef]
44. Hashimoto, K.; Irie, H.; Fujishima, A. TiO_2 Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **2005**, *44*, 8269. [CrossRef]
45. Fujishima, A.; Hashimoto, K.; Watanabe, T. *TiO_2 Photocatalysis: Fundamentals and Applications*; Bkc: Tokyo, Japan, 1999.
46. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96. [CrossRef]
47. de Richter, R.; Caillol, S. Fighting Global Warming: The Potential of Photocatalysis against CO_2, CH_4, N_2O, CFCs, Tropospheric O_3, BC and Other Major Contributors to Climate Change. *J. Photochem. Photobiol. C Photochem. Rev.* **2011**, *12*, 1–19. [CrossRef]
48. Mo, J.; Zhang, Y.; Xu, Q.; Lamson, J.J.; Zhao, R. Photocatalytic Purification of Volatile Organic Compounds in Indoor Air: A Literature Review. *Atmos. Environ.* **2009**, *43*, 2229–2246. [CrossRef]
49. ISO 22197-1:2007. 2007. Available online: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data\/standard/04/07/40761.html (accessed on 20 May 2021).
50. ISO/TC 206 Fine ceramics. ISO 22197-1:2016. 2016. Available online: https://www.iso.org/cms/render/live/en/sites/isoorg/\contents/data/standard/06/54/65416.html (accessed on 20 May 2021).
51. Motohashi, K.; Dehn, F.; Ohama, Y. Standardization of Testing Methods for Construction Materials with TiO_2 Photocatalyst. In *Applications of Titanium Dioxide Photocatalysis to Construction Materials: State-of-the-Art Report of the RILEM Technical Committee 194-TDP*; Ohama, Y., Van Gemert, D., Eds.; RILEM State of the Art Reports; Springer: Dordrecht, The Netherlands, 2011; pp. 37–41. [CrossRef]
52. Khanal, V.; Balayeva, N.O.; Günnemann, C.; Mamiyev, Z.; Dillert, R.; Bahnemann, D.W.; Subramanian, V.R. Photocatalytic NOx Removal Using Tantalum Oxide Nanoparticles: A Benign Pathway. *Appl. Catal. B Environ.* **2021**, *291*, 119974. [CrossRef]
53. Freitag, J.; Domínguez, A.; Niehaus, T.A.; Hülsewig, A.; Dillert, R.; Frauenheim, T.; Bahnemann, D.W. Nitrogen(II) Oxide Charge Transfer Complexes on TiO_2: A New Source for Visible-Light Activity. *J. Phys. Chem. C* **2015**, *119*, 4488–4501. [CrossRef]
54. Balayeva, N.O.; Fleisch, M.; Bahnemann, D.W. Surface-Grafted WO_3/TiO_2 Photocatalysts: Enhanced Visible-Light Activity towards Indoor Air Purification. *Catal. Today* **2018**, *313*, 63–71. [CrossRef]
55. Chen, M.; Chu, J.W. NOx Photocatalytic Degradation on Active Concrete Road Surface—From Experiment to Real-Scale Application. *J. Clean. Prod.* **2011**, *19*, 1266–1272. [CrossRef]
56. Folli, A.; Strøm, M.; Madsen, T.P.; Henriksen, T.; Lang, J.; Emenius, J.; Klevebrant, T.; Nilsson, Å. Field Study of Air Purifying Paving Elements Containing TiO_2. *Atmos. Environ.* **2015**, *107*, 44–51. [CrossRef]

57. Hassan, M.; Mohammad, L.N.; Asadi, S.; Dylla, H.; Cooper, S. Sustainable Photocatalytic Asphalt Pavements for Mitigation of Nitrogen Oxide and Sulfur Dioxide Vehicle Emissions. *J. Mater. Civ. Eng.* **2013**, *25*, 365–371. [CrossRef]
58. Hüsken, G.; Hunger, M.; Brouwers, H.J.H. Experimental Study of Photocatalytic Concrete Products for Air Purification. *Build. Environ.* **2009**, *44*, 2463–2474. [CrossRef]
59. de Melo, J.V.S.; Trichês, G. Evaluation of the Influence of Environmental Conditions on the Efficiency of Photocatalytic Coatings in the Degradation of Nitrogen Oxides (NOx). *Build. Environ.* **2012**, *49*, 117–123. [CrossRef]
60. Dillert, R.; Stötzner, J.; Engel, A.; Bahnemann, D.W. Influence of Inlet Concentration and Light Intensity on the Photocatalytic Oxidation of Nitrogen(II) Oxide at the Surface of Aeroxide® TiO_2 P25. *J. Hazard. Mater.* **2012**, *211–212*, 240–246. [CrossRef]
61. Herrmann, J.M.; Péruchon, L.; Puzenat, E.; Guillard, C. Photocatalysis: From fundamentals to self-cleaning glass application. In *International RILEM Symposium on Photocatalysis, Environment and Construction Materials*; RILEM Publications SARL: Paris, France, 2007; pp. 8–9.
62. Jacoby, W.A.; Blake, D.M.; Noble, R.D.; Koval, C.A. Kinetics of the Oxidation of Trichloroethylene in Air via Heterogeneous Photocatalysis. *J. Catal.* **1995**, *157*, 87–96. [CrossRef]
63. Lim, T.H.; Jeong, S.M.; Kim, S.D.; Gyenis, J. Photocatalytic Decomposition of NO by TiO_2 Particles. *J. Photochem. Photobiol. A Chem.* **2000**, *134*, 209–217. [CrossRef]
64. Peral, J.; Ollis, D.F. Heterogeneous Photocatalytic Oxidation of Gas-Phase Organics for Air Purification: Acetone, 1-Butanol, Butyraldehyde, Formaldehyde, and m-Xylene Oxidation. *J. Catal.* **1992**, *136*, 554–565. [CrossRef]
65. Hunger, M.; Hüsken, G.; Brouwers, H. Photocatalytic Degradation of Air Pollutants—From Modeling to Large Scale Application. *Cem. Concr. Res.* **2010**, *40*, 313–320. [CrossRef]
66. Gallus, M.; Akylas, V.; Barmpas, F.; Beeldens, A.; Boonen, E.; Boréave, A.; Cazaunau, M.; Chen, H.; Daële, V.; Doussin, J.F.; et al. Photocatalytic De-Pollution in the Leopold II Tunnel in Brussels: NOx Abatement Results. *Build. Environ.* **2015**, *84*, 125–133. [CrossRef]
67. Zouzelka, R.; Rathousky, J. Photocatalytic Abatement of NOx Pollutants in the Air Using Commercial Functional Coating with Porous Morphology. *Appl. Catal. B Environ.* **2017**, *217*, 466–476. [CrossRef]
68. Rhee, I.; Lee, J.S.; Kim, J.; Kim, J.H. Nitrogen Oxides Mitigation Efficiency of Cementitious Materials Incorporated with TiO_2. *Materials* **2018**, *11*, 877. [CrossRef] [PubMed]
69. Ballari, M.M.; Brouwers, H.J.H. Full Scale Demonstration of Air-Purifying Pavement. *J. Hazard. Mater.* **2013**, *254–255*, 406–414. [CrossRef] [PubMed]
70. Gallus, M.; Ciuraru, R.; Mothes, F.; Akylas, V.; Barmpas, F.; Beeldens, A.; Bernard, F.; Boonen, E.; Boréave, A.; Cazaunau, M.; et al. Photocatalytic Abatement Results from a Model Street Canyon. *Environ. Sci. Pollut. Res.* **2015**, *22*, 18185–18196. [CrossRef] [PubMed]
71. Martinez, T.; Bertron, A.; Ringot, E.; Escadeillas, G. Degradation of NO Using Photocatalytic Coatings Applied to Different Substrates. *Build. Environ.* **2011**, *46*, 1808–1816. [CrossRef]
72. Araña, J.; Garzón Sousa, D.; González Díaz, O.; Pulido Melián, E.; Doña Rodríguez, J.M. Effect of NO_2 and NO_3^-/HNO_3 Adsorption on NO Photocatalytic Conversion. *Appl. Catal. B Environ.* **2019**, *244*, 660–670. [CrossRef]
73. Maggos, T.; Bartzis, J.G.; Liakou, M.; Gobin, C. Photocatalytic Degradation of NOx Gases Using TiO_2-Containing Paint: A Real Scale Study. *J. Hazard. Mater.* **2007**, *146*, 668–673. [CrossRef]
74. Ao, C.H.; Lee, S.C.; Mak, C.L.; Chan, L.Y. Photodegradation of Volatile Organic Compounds (VOCs) and NO for Indoor Air Purification Using TiO_2: Promotion versus Inhibition Effect of NO. *Appl. Catal. B Environ.* **2003**, *42*, 119–129. [CrossRef]
75. Ao, C.H.; Lee, S.C.; Zou, S.C.; Mak, C.L. Inhibition Effect of SO_2 on NOx and VOCs during the Photodegradation of Synchronous Indoor Air Pollutants at Parts per Billion (ppb) Level by TiO_2. *Appl. Catal. B Environ.* **2004**, *49*, 187–193. [CrossRef]
76. de Melo, J.V.S.; Trichês, G.; Gleize, P.J.P.; Villena, J. Development and Evaluation of the Efficiency of Photocatalytic Pavement Blocks in the Laboratory and after One Year in the Field. *Constr. Build. Mater.* **2012**, *37*, 310–319. [CrossRef]
77. Osborn, D.; Hassan, M.; Asadi, S.; White, J.R. Durability Quantification of TiO_2 Surface Coating on Concrete and Asphalt Pavements. *J. Mater. Civ. Eng.* **2014**, *26*, 331–337. [CrossRef]
78. Jiménez-Relinque, E.; Hingorani, R.; Rubiano, F.; Grande, M.; Castillo, Á.; Castellote, M. In Situ Evaluation of the NOx Removal Efficiency of Photocatalytic Pavements: Statistical Analysis of the Relevance of Exposure Time and Environmental Variables. *Environ. Sci. Pollut. Res.* **2019**, *26*, 36088–36095. [CrossRef]
79. Kaja, A.M.; Brouwers, H.J.H.; Yu, Q.L. NOx Degradation by Photocatalytic Mortars: The Underlying Role of the CH and C-S-H Carbonation. *Cem. Concr. Res.* **2019**, *125*, 105805. [CrossRef]
80. Poon, C.S.; Cheung, E. NO Removal Efficiency of Photocatalytic Paving Blocks Prepared with Recycled Materials. *Constr. Build. Mater.* **2007**, *21*, 1746–1753. [CrossRef]
81. Jimenez-Relinque, E.; Rodriguez-Garcia, J.R.; Castillo, A.; Castellote, M. Characteristics and Efficiency of Photocatalytic Cementitious Materials: Type of Binder, Roughness and Microstructure. *Cem. Concr. Res.* **2015**, *71*, 124–131. [CrossRef]
82. Pérez-Nicolás, M.; Balbuena, J.; Cruz-Yusta, M.; Sánchez, L.; Navarro-Blasco, I.; Fernández, J.M.; Alvarez, J.I. Photocatalytic NOx Abatement by Calcium Aluminate Cements Modified with TiO_2: Improved NO_2 Conversion. *Cem. Concr. Res.* **2015**, *70*, 67–76. [CrossRef]
83. Gauvin, F.; Caprai, V.; Yu, Q.L.; Brouwers, H.J.H. Effect of the Morphology and Pore Structure of Porous Building Materials on Photocatalytic Oxidation of Air Pollutants. *Appl. Catal. B Environ.* **2018**, *227*, 123–131. [CrossRef]

84. Fan, W.; Chan, K.Y.; Zhang, C.; Zhang, K.; Ning, Z.; Leung, M.K.H. Solar Photocatalytic Asphalt for Removal of Vehicular NOx: A Feasibility Study. *Appl. Energy* **2018**, *225*, 535–541. [CrossRef]
85. Witkowski, H.; Jackiewicz-Rek, W.; Chilmon, K.; Jarosławski, J.; Tryfon-Bojarska, A.; Gąsiński, A. Air Purification Performance of Photocatalytic Concrete Paving Blocks after Seven Years of Service. *Appl. Sci.* **2019**, *9*, 1735. [CrossRef]
86. Shi, X.; Wang, P.; Li, W.; Bai, Y.; Xie, H.; Zhou, Y.; Ye, L. Change in Photocatalytic NO Removal Mechanisms of Ultrathin BiOBr/BiOI via NO_3^- Adsorption. *Appl. Catal. B Environ.* **2019**, *243*, 322–329. [CrossRef]
87. Nguyen, N.H.; Bai, H. Photocatalytic Removal of NO and NO_2 Using Titania Nanotubes Synthesized by Hydrothermal Method. *J. Environ. Sci.* **2014**, *26*, 1180–1187. [CrossRef]
88. Sheng, Z.; Wu, Z.; Liu, Y.; Wang, H. Gas-Phase Photocatalytic Oxidation of NO over Palladium Modified TiO_2 Catalysts. *Catal. Commun.* **2008**, *9*, 1941–1944. [CrossRef]
89. Boonen, E.; Akylas, V.; Barmpas, F.; Boréave, A.; Bottalico, L.; Cazaunau, M.; Chen, H.; Daële, V.; De Marco, T.; Doussin, J.F.; et al. Construction of a Photocatalytic De-Polluting Field Site in the Leopold II Tunnel in Brussels. *J. Environ. Manag.* **2015**, *155*, 136–144. [CrossRef] [PubMed]
90. Chen, M.; Liu, Y. NOx Removal from Vehicle Emissions by Functionality Surface of Asphalt Road. *J. Hazard. Mater.* **2010**, *174*, 375–379. [CrossRef]
91. Castellote, M. Device for Determining Photocatalytic Properties of Materials. WO Patent 2017085342 A1, 26 May 2017.
92. Hunger, M.; Brouwers, H. Comparative Study on Cementitious Products Containing Titanium Dioxide as Photo-Catalyst. In Proceedings of the International RILEM Symposium on Photocatalysis, Environment and Construction Materials, Florence, Italy, 8–9 October 2007.
93. Murata, Y.; Obata, H.; Tawara, H.; Murata, K. NOx-Cleaning Paving Block. U.S. Patent US5861205A, 19 January 1999.
94. Cassar, L.; Cucitore, R.; Pepe, C. Cement-Based Paving Blocks for Photocatalytic Paving for the Abatement of Urban Pollutants. U.S. Patent US7960042B2, 14 June 2011.
95. Ma, J.; Wu, H.; Liu, Y.; He, H. Photocatalytic Removal of NOx over Visible Light Responsive Oxygen-Deficient TiO_2. *J. Phys. Chem. C* **2014**, *118*, 7434–7441. [CrossRef]
96. Pérez-Nicolás, M.; Navarro-Blasco, I.; Fernández, J.M.; Alvarez, J.I. Atmospheric NOx Removal: Study of Cement Mortars with Iron- and Vanadium-Doped TiO_2 as Visible Light–Sensitive Photocatalysts. *Constr. Build. Mater.* **2017**, *149*, 257–271. [CrossRef]
97. Xu, H.; Ouyang, S.; Liu, L.; Reunchan, P.; Umezawa, N.; Ye, J. Recent Advances in TiO_2-Based Photocatalysis. *J. Mater. Chem. A* **2014**, *2*, 12642–12661. [CrossRef]
98. Martinez-Oviedo, A. Enhancement of NOx Photo-Oxidation by Fe- and Cu-Doped Blue TiO_2. *Environ. Sci. Pollut. Res.* **2020**, *27*, 26702–26713. [CrossRef]
99. Ma, J.; He, H.; Liu, F. Effect of Fe on the Photocatalytic Removal of NOx over Visible Light Responsive Fe/TiO_2 Catalysts. *Appl. Catal. B Environ.* **2015**, *179*, 21–28. [CrossRef]
100. Balbuena, J.; Carraro, G.; Cruz, M.; Gasparotto, A.; Maccato, C.; Pastor, A.; Sada, C.; Barreca, D.; Sánchez, L. Advances in Photocatalytic NOx Abatement through the Use of Fe_2O_3/TiO_2 Nanocomposites. *RSC Adv.* **2016**, *6*, 74878–74885. [CrossRef]
101. Martinez-Oviedo, A.; Ray, S.K.; Nguyen, H.P.; Lee, S.W. Efficient Photo-Oxidation of NOx by Sn Doped Blue TiO_2 Nanoparticles. *J. Photochem. Photobiol. A Chem.* **2019**, *370*, 18–25. [CrossRef]
102. Zhao, Y.; Li, C.; Liu, X.; Gu, F.; Du, H.L.; Shi, L. Zn-Doped TiO_2 Nanoparticles with High Photocatalytic Activity Synthesized by Hydrogen–Oxygen Diffusion Flame. *Appl. Catal. B Environ.* **2008**, *79*, 208–215. [CrossRef]
103. Papoulis, D.; Somalakidi, K.; Todorova, N.; Trapalis, C.; Panagiotaras, D.; Sygkridou, D.; Stathatos, E.; Gianni, E.; Mavrikos, A.; Komarneni, S. Sepiolite/TiO_2 and Metal Ion Modified Sepiolite/TiO_2 Nanocomposites: Synthesis, Characterization and Photocatalytic Activity in Abatement of NOx Gases. *Appl. Clay Sci.* **2019**, *179*, 105156. [CrossRef]
104. Luna, M.; Gatica, J.M.; Vidal, H.; Mosquera, M.J. Au-TiO_2/SiO_2 Photocatalysts with NOx Depolluting Activity: Influence of Gold Particle Size and Loading. *Chem. Eng. J.* **2019**, *368*, 417–427. [CrossRef]
105. Soylu, A.M.; Polat, M.; Erdogan, D.A.; Say, Z.; Yıldırım, C.; Birer, Ö.; Ozensoy, E. TiO_2–Al_2O_3 Binary Mixed Oxide Surfaces for Photocatalytic NOx Abatement. *Appl. Surf. Sci.* **2014**, *318*, 142–149. [CrossRef]
106. Fujiwara, K.; Pratsinis, S.E. Atomically Dispersed Pd on Nanostructured TiO_2 for NO Removal by Solar Light. *AIChE J.* **2017**, *63*, 139–146. [CrossRef]
107. Hu, Y.; Song, X.; Jiang, S.; Wei, C. Enhanced Photocatalytic Activity of Pt-Doped TiO_2 for NOx Oxidation Both under UV and Visible Light Irradiation: A Synergistic Effect of Lattice Pt^{4+} and Surface PtO. *Chem. Eng. J.* **2015**, *274*, 102–112. [CrossRef]
108. Hernández Rodríguez, M.J.; Pulido Melián, E.; García Santiago, D.; González Díaz, O.; Navío, J.A.; Doña Rodríguez, J.M. NO Photooxidation with TiO_2 Photocatalysts Modified with Gold and Platinum. *Appl. Catal. B Environ.* **2017**, *205*, 148–157. [CrossRef]
109. Xu, M.; Wang, Y.; Geng, J.; Jing, D. Photodecomposition of NOx on Ag/TiO_2 Composite Catalysts in a Gas Phase Reactor. *Chem. Eng. J.* **2017**, *307*, 181–188. [CrossRef]
110. Tobaldi, D.M.; Hortigüela Gallo, M.J.; Otero-Irurueta, G.; Singh, M.K.; Pullar, R.C.; Seabra, M.P.; Labrincha, J.A. Purely Visible-Light-Induced Photochromism in Ag–TiO_2 Nanoheterostructures. *Langmuir* **2017**, *33*, 4890–4902. [CrossRef] [PubMed]
111. Ma, J.; Wang, C.; He, H. Enhanced Photocatalytic Oxidation of NO over G-C_3N_4-TiO_2 under UV and Visible Light. *Appl. Catal. B Environ.* **2016**, *184*, 28–34. [CrossRef]
112. Papailias, I.; Todorova, N.; Giannakopoulou, T.; Yu, J.; Dimotikali, D.; Trapalis, C. Photocatalytic Activity of Modified G-C_3N_4/TiO_2 Nanocomposites for NOx Removal. *Catal. Today* **2017**, *280*, 37–44. [CrossRef]

113. Trapalis, A.; Todorova, N.; Giannakopoulou, T.; Boukos, N.; Speliotis, T.; Dimotikali, D.; Yu, J. TiO_2/Graphene Composite Photocatalysts for NOx Removal: A Comparison of Surfactant-Stabilized Graphene and Reduced Graphene Oxide. *Appl. Catal. B Environ.* **2016**, *180*, 637–647. [CrossRef]
114. Lu, X.; Song, C.; Jia, S.; Tong, Z.; Tang, X.; Teng, Y. Low-Temperature Selective Catalytic Reduction of NOx with NH_3 over Cerium and Manganese Oxides Supported on TiO_2–Graphene. *Chem. Eng. J.* **2015**, *260*, 776–784. [CrossRef]
115. Huang, Y.; Chen, D.; Hu, X.; Qian, Y.; Li, D. Preparation of TiO_2/Carbon Nanotubes/Reduced Graphene Oxide Composites with Enhanced Photocatalytic Activity for the Degradation of Rhodamine B. *Nanomaterials* **2018**, *8*, 431. [CrossRef]
116. Todorova, N.; Giannakopoulou, T.; Karapati, S.; Petridis, D.; Vaimakis, T.; Trapalis, C. Composite TiO_2/Clays Materials for Photocatalytic NOx Oxidation. *Appl. Surf. Sci.* **2014**, *319*, 113–120. [CrossRef]
117. Folli, A. Properties and Photochemistry of Valence-Induced-Ti^{3+} Enriched (Nb,N)-Codoped Anatase TiO_2 Semiconductors. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4849–4853. [CrossRef]
118. Folli, A.; Bloh, J.Z.; Beukes, E.P.; Howe, R.F.; Macphee, D.E. Photogenerated Charge Carriers and Paramagnetic Species in (W,N)-Codoped TiO_2 Photocatalysts under Visible-Light Irradiation: An EPR Study. *J. Phys. Chem. C* **2013**, *117*, 22149–22155. [CrossRef]
119. Folli, A.; Bloh, J.; Macphee, D. Band Structure and Charge Carrier Dynamics in (W,N)-Codoped TiO_2 Resolved by Electrochemical Impedance Spectroscopy Combined with UV–Vis and EPR Spectroscopies. *J. Electroanal. Chem.* **2016**, *780*, 367–372. [CrossRef]
120. Bloh, J.Z.; Folli, A.; Macphee, D.E. Adjusting Nitrogen Doping Level in Titanium Dioxide by Codoping with Tungsten: Properties and Band Structure of the Resulting Materials. *J. Phys. Chem. C* **2014**, *118*, 21281–21292. [CrossRef]
121. Fujiwara, K.; Pratsinis, S.E. Single Pd Atoms on TiO_2 Dominate Photocatalytic NOx Removal. *Appl. Catal. B Environ.* **2018**, *226*, 127–134. [CrossRef]
122. Fujiwara, K.; Müller, U.; Pratsinis, S.E. Pd Subnano-Clusters on TiO_2 for Solar-Light Removal of NO. *ACS Catal.* **2016**, *6*, 1887–1893. [CrossRef]
123. Nava-Núñez, M.Y.; Jimenez-Relinque, E.; Grande, M.; Martínez-de la Cruz, A.; Castellote, M. Photocatalytic BiOX Mortars under Visible Light Irradiation: Compatibility, NOx Efficiency and Nitrate Selectivity. *Catalysts* **2020**, *10*, 226. [CrossRef]
124. Yang, Y.; Ji, T.; Su, W.; Yang, B.; Zhang, Y.; Yang, Z. Photocatalytic NOx Abatement and Self-Cleaning Performance of Cementitious Composites with g-C_3N_4 Nanosheets under Visible Light. *Constr. Build. Mater.* **2019**, *225*, 120–131. [CrossRef]
125. Jin, Q.; Saad, E.M.; Zhang, W.; Tang, Y.; Kurtis, K.E. Quantification of NOx Uptake in Plain and TiO_2-Doped Cementitious Materials. *Cem. Concr. Res.* **2019**, *122*, 251–256. [CrossRef]
126. Fan, W.; Chan, K.Y.; Zhang, C.; Leung, M.K.H. Advanced Solar Photocatalytic Asphalt for Removal of Vehicular NOx. *Energy Procedia* **2017**, *143*, 811–816. [CrossRef]
127. Tawari, A.; Einicke, W.D.; Gläser, R. Photocatalytic Oxidation of NO over Composites of Titanium Dioxide and Zeolite ZSM-5. *Catalysts* **2016**, *6*, 31. [CrossRef]
128. Ao, C.H.; Lee, S.C. Combination Effect of Activated Carbon with TiO_2 for the Photodegradation of Binary Pollutants at Typical Indoor Air Level. *J. Photochem. Photobiol. A Chem.* **2004**, *161*, 131–140. [CrossRef]
129. Folli, A.; Pochard, I.; Nonat, A.; Jakobsen, U.H.; Shepherd, A.M.; Macphee, D.E. Engineering Photocatalytic Cements: Understanding TiO_2 Surface Chemistry to Control and Modulate Photocatalytic Performances. *J. Am. Ceram. Soc.* **2010**, *93*, 3360–3369. [CrossRef]
130. Final Report Summary—LIGHT2CAT (Visible LIGHT Active PhotoCATalytic Concretes for Air Pollution Treatment) | Report Summary | FP7. 2015. Available online: https://cordis.europa.eu/project/id/283062/reporting (accessed on 20 May 2021).
131. Folli, A.; Bloh, J.Z.; Strøm, M.; Pilegaard Madsen, T.; Henriksen, T.; Macphee, D.E. Efficiency of Solar-Light-Driven TiO_2 Photocatalysis at Different Latitudes and Seasons. Where and When Does TiO_2 Really Work? *J. Phys. Chem. Lett.* **2014**, *5*, 830–832. [CrossRef]
132. Poulsen, S.; Svec, O.; Kaasgaard, M.; Folli, A. *Visible LIGHT Active PhotoCATalytic Concretes for Air Pollution Treatment*; Technical Report Version 2; DTI: Taastrup, Denmark, 2016.
133. Flassak, T. Numerical simulation of the depollution effectiveness of photocatalytic coverings in street canyons. In Proceedings of the Photocatalysis: Science and Application for Urban Air Quality, The LIFE+ PhotoPaq Conference, Corse, France, 14–17 May 2012.
134. Bolte, G.; Flassak, T. Numerical simulation of the effectiveness of photocatalytically active concrete surfaces. *Int. Build. Mater. Conf.* **2012**, *18*, 548–558.
135. Guerrini, G.L.; Peccati, E. Photocatalytic Cementitious Roads for Depollution. In Proceedings of the International RILEM Symposium on Photocatalysis, Environment and Construction Materials, Florence, 8–9 October 2007.
136. Suárez, S.; Portela, R.; Hernández-Alonso, M.D.; Sánchez, B. Development of a Versatile Experimental Setup for the Evaluation of the Photocatalytic Properties of Construction Materials under Realistic Outdoor Conditions. *Environ. Sci. Pollut. Res.* **2014**, *21*, 11208–11217. [CrossRef]
137. Borlaza, L.J.S. Evaluation of the Efficiency of an Ultrafine Titanium Dioxide—Based Paint for Removing Nitrogen Oxides in an Indoor and Outdoor Environment. Master's Thesis, Manila University, Metro Manila, Philippines, 2012.
138. Kim, Y.K.; Hong, S.J.; Kim, H.B.; Lee, S.W. Evaluation of In-Situ NOx Removal Efficiency of Photocatalytic Concrete in Expressways. *KSCE J. Civ. Eng.* **2018**, *22*, 2274–2280. [CrossRef]
139. Tremper, A.; Green, D. *Artworks D-NOX Paint Trial Report*; Technical Report; King's College London: London, UK, 2016.

140. IPL. *Dutch Air Quality Innovation Programme Concluded*; Technical Report; Rijkswaterstaat: Utrecht, The Netherlands, 2010.
141. Maggos, T.; Plassais, A.; Bartzis, J.G.; Vasilakos, C.; Moussiopoulos, N.; Bonafous, L. Photocatalytic Degradation of NOx in a Pilot Street Canyon Configuration Using TiO_2-Mortar Panels. *Environ. Monit. Assess.* **2008**, *136*, 35–44. [CrossRef]
142. Barratt, B. *CoL De-Nox Paint Statistical Report*; Technical Report; King's College London: London, UK, 2007.
143. Barratt, B.; Carslaw, D.; Green, D. *High Holborn D-NOx Paint Trial –Report 3 (Updated)*; Client: London Borough of Camden Report 3; King's College London: London, UK, 2012.
144. Ifang, S.; Gallus, M.; Liedtke, S.; Kurtenbach, R.; Wiesen, P.; Kleffmann, J. Standardization Methods for Testing Photo-Catalytic Air Remediation Materials: Problems and Solution. *Atmos. Environ.* **2014**, *91*, 154–161. [CrossRef]
145. Colvile, R.; Barmpas, P.; Ossanlis, I.; Moussiopoulos, N. *Assessment of the Effectiveness of NOx Absorbing Paint at the Sir John Cass Primary School*; Technical Report; Imperial College: London, UK, 2007.
146. Guerrini, G.L. Photocatalytic Performances in a City Tunnel in Rome: NOx Monitoring Results. *Constr. Build. Mater.* **2012**, *27*, 165–175. [CrossRef]
147. Kerrod, J.; McIntyre, R. *The Effectiveness of CristalACTiV™ for Depollution in Tunnels with Low Levels of Light*; Technical Report; Cristal, R&D: Lincolnshire, UK, 2014.
148. Guerrini, G.L.; Peccati, E. *TUNNEL "UMBERTO I", IN ROME Monitoring Program Results*; Technical Report 24; CTG Italcementi Group: Bergamo, Italy, 2008.
149. Dylla, H.; Asadi, S.; Hassan, M.; Mohammad, L.N. Evaluating Photocatalytic Asphalt Pavement Effectiveness in Real-World Environments through Developing Models: A Statistical and Kinetic Study. *Road Mater. Pavement Des.* **2013**, *14*, 92–105. [CrossRef]
150. Jiang, Z.; Yu, X.B. Impact of Visible-Solar-Light-Driven Photocatalytic Pavement on Air Quality Improvement. *Transp. Res. Part D Transp. Environ.* **2020**, *84*, 102341. [CrossRef]
151. de O.B. Lira, J.; Padoin, N.; Vilar, V.J.P.; Soares, C. Photocatalytic NOx Abatement: Mathematical Modeling, CFD Validation and Reactor Analysis. *J. Hazard. Mater.* **2019**, *372*, 145–153. [CrossRef] [PubMed]
152. Ballari, M.M.; Hunger, M.; Hüsken, G.; Brouwers, H.J.H. Modelling and Experimental Study of the NOx Photocatalytic Degradation Employing Concrete Pavement with Titanium Dioxide. *Catal. Today* **2010**, *151*, 71–76. [CrossRef]
153. Moussiopoulos, N.; Barmpas, P.; Ossanlis, I.; Bartzis, J. Comparison of Numerical and Experimental Results for the Evaluation of the Depollution Effectiveness of Photocatalytic Coverings in Street Canyons. *Environ. Model. Assess.* **2008**, *13*, 357–368. [CrossRef]
154. Simmons, A.J.; Willett, K.M.; Jones, P.D.; Thorne, P.W.; Dee, D.P. Low-Frequency Variations in Surface Atmospheric Humidity, Temperature, and Precipitation: Inferences from Reanalyses and Monthly Gridded Observational Data Sets. *J. Geophys. Res.* **2010**, *115*, D01110. [CrossRef]
155. Carslaw, D. Evidence of an Increasing NO_2/NOx Emissions Ratio from Road Traffic Emissions. *Atmos. Environ.* **2005**, *39*, 4793–4802. [CrossRef]
156. Chen, J.; Kou, S.C.; Poon, C.S. Photocatalytic Cement-Based Materials: Comparison of Nitrogen Oxides and Toluene Removal Potentials and Evaluation of Self-Cleaning Performance. *Build. Environ.* **2011**, *46*, 1827–1833. [CrossRef]
157. Bloh, J.Z.; Folli, A.; Macphee, D.E. Photocatalytic NOx Abatement: Why the Selectivity Matters. *RSC Adv.* **2014**, *4*, 45726–45734. [CrossRef]
158. Ângelo, J.; Andrade, L.; Mendes, A. Highly Active Photocatalytic Paint for NOx Abatement under Real-Outdoor Conditions. *Appl. Catal. A Gen.* **2014**, *484*, 17–25. [CrossRef]
159. Sofianou, M.V.; Psycharis, V.; Boukos, N.; Vaimakis, T.; Yu, J.; Dillert, R.; Bahnemann, D.; Trapalis, C. Tuning the Photocatalytic Selectivity of TiO_2 Anatase Nanoplates by Altering the Exposed Crystal Facets Content. *Appl. Catal. B Environ.* **2013**, *142–143*, 761–768. [CrossRef]
160. Shelimov, B.N.; Tolkachev, N.N.; Tkachenko, O.P.; Baeva, G.N.; Klementiev, K.V.; Stakheev, A.Y.; Kazansky, V.B. Enhancement Effect of TiO_2 Dispersion over Alumina on the Photocatalytic Removal of NOx Admixtures from O_2–N_2 Flow. *J. Photochem. Photobiol. A Chem.* **2008**, *195*, 81–88. [CrossRef]
161. Devahasdin, S.; Fan, C.; Li, K.; Chen, D.H. TiO_2 Photocatalytic Oxidation of Nitric Oxide: Transient Behavior and Reaction Kinetics. *J. Photochem. Photobiol. A Chem.* **2003**, *156*, 161–170. [CrossRef]
162. Folli, A.; Campbell, S.B.; Anderson, J.A.; Macphee, D.E. Role of TiO_2 Surface Hydration on NO Oxidation Photo-Activity. *J. Photochem. Photobiol. A Chem.* **2011**, *220*, 85–93. [CrossRef]
163. Ohko, Y.; Nakamura, Y.; Negishi, N.; Matsuzawa, S.; Takeuchi, K. Photocatalytic Oxidation of Nitrogen Monoxide Using TiO_2 Thin Films under Continuous UV Light Illumination. *J. Photochem. Photobiol. A Chem.* **2009**, *205*, 28–33. [CrossRef]
164. Wu, Q.; van de Krol, R. Selective Photoreduction of Nitric Oxide to Nitrogen by Nanostructured TiO_2 Photocatalysts: Role of Oxygen Vacancies and Iron Dopant. *J. Am. Chem. Soc.* **2012**, *134*, 9369–9375. [CrossRef]
165. Polat, M.; Soylu, A.M.; Erdogan, D.A.; Erguven, H.; Vovk, E.I.; Ozensoy, E. Influence of the Sol–Gel Preparation Method on the Photocatalytic NO Oxidation Performance of TiO_2/Al_2O_3 Binary Oxides. *Catal. Today* **2015**, *241*, 25–32. [CrossRef]
166. Lewis, R.J.; Sax, N. *Sax's Dangerous Properties of Industrial Materials*; John Wiley & Sons: New York, NY, USA, 1996; Volume 8.
167. Pepin, L. *Etude In Situ des Propriétés Purificatrices de Revêtements Photocatalytiques sur la Pollution Atmosphérique*; Technical Report 1; TERA Environment: Rhône-Alpes, France, 2009.
168. Jimenez-Relinque, E.; Castellote, M. Quick Assessment of the Photocatalytic Activity of TiO_2 Construction Materials by Nitroblue Tetrazolium (NBT) Ink. *Constr. Build. Mater.* **2019**, *214*, 1–8. [CrossRef]

169. Gandolfo, A.; Bartolomei, V.; Gomez Alvarez, E.; Tlili, S.; Gligorovski, S.; Kleffmann, J.; Wortham, H. The Effectiveness of Indoor Photocatalytic Paints on NOx and HONO Levels. *Appl. Catal. B Environ.* **2015**, *166–167*, 84–90. [CrossRef]