THE UNIVERSITY OF TEXAS AT AUSTIN
CENTER FOR TRANSPORTATION RESEARCH

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# Literature Review on Use of Nanoparticle Technology for Reducing Emissions

Lisa Loftus-Otway

August 2019; Published July 2021

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16. Abstract

Nanoscale science, engineering, chemistry and technology—nanotechnology science—is expected to deliver societal and economic benefits in multiple fields. Transportation is expected to be one of the sectors that will see impacts from improved material life through to environmental benefits. This report provides a high-level overview and introduction to the science of nanotechnology, reviews the federal role and funding for nanotechnology, and outlines national-level research, initiatives, and organizations. Also provided is a high-level overview of current topics of nanotechnology research and development (R&D) in transportation infrastructure, including its use to achieve emissions reductions.

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Lisa Loftus-Otway



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# Chapter 1. Summary

Nanoscale science, engineering, chemistry, and technology—which the Congressional Research Service in a 2016 primer (CRS, 2016) refers to "nanotechnology science"—is expected to deliver societal and economic benefits in multiple fields. Transportation is expected to be one of the sectors that will see impacts from improved material life through to environmental benefits.

Nanotechnology operates at the scale of 1 to 100 nanometers (one nanometer = billionth of a meter). Properties of matter at this size are fundamentally different than the properties of individual atoms and molecules. Nanoscale materials have far larger surface areas than similar masses of larger-scale materials. This means that as surface area per mass of a material increases at the nanoscale, a greater amount of the nanoscale material can come into contact with surrounding materials, thus affecting reactivity. In the case of titanium dioxide ($TiO_2$) applied to concrete to create photocatalytic concrete, this greater surface area allows the remediation of carbon dioxide ($CO_2$), nitrogen oxides ($NO_x$), and other chemicals when the surface is exposed to ultraviolet (UV) rays from sunlight. When rain (or water that is applied) reacts with the $TiO_2$ and UV light, it undergoes a chemical change and allows the pollutants to, in essence, wash away.

Nanotechnology is derived from two main approaches: the "top-down" approach, wherein larger structures are reduced in size to the nanoscale but maintain their original properties without atomic-level control (for example, electronics miniaturization) or are deconstructed from larger structures into their smaller, composite parts; and secondly the ''bottom-up" approach, also called "molecular nanotechnology" or ''molecular manufacturing," wherein materials are engineered from atoms or molecular components through a process of assembly/self-assembly

Much of the current technology developments and applications are incremental—some say evolutionary—in nature, offering what seem like very modest improvements. Nanotechnology is playing a current substantive fundamental role in microchips and storage density of memory in computing.

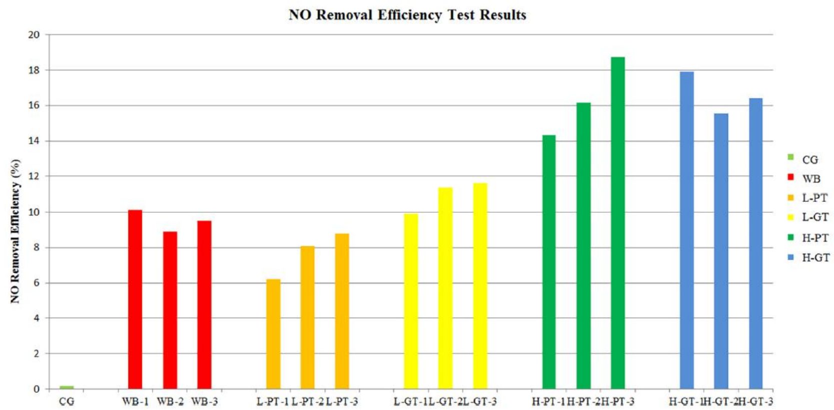
At the federal level, the United States Congress began supporting research and development (R&D) in 2000. Funding began in 2001 when the U.S. Congress appropriated just under $500 million for agencies conducting nanotechnology work. In 2003 the U.S. Congress passed the 21st Century Nanotechnology Research and Development Act of 2003 (Public Law 108-153, 15 USC §7501). The law authorized the legislative foundation for the National Nanotechnology Initiative (NNI). The President's 2018 budget provided for $1.2 billion in support to the NNI. Nanotechnology research has been directed to three major topic areas: federal R&D investments, U.S. international competitiveness and environment, and health and safety concerns. According to the Congressional Research Service, the U.S. is estimated to account for approximately a third of total global nanotechnology R&D.

To date there has been a plethora of research into nanotechnology in multiple fields. For nanotechnology specifically in transportation and emissions reduction, much of the focus has been on tailpipe emission reduction through the use of nanomaterials. For the purposes of this literature review, however, research into nanotechnology for use in transportation infrastructure to gain emissions reductions has primarily focused on concrete and the use of nano TiO2.

The literature review went through an interactive process. The CTR library staff (who assisted in this process) used databases at UT Austin and found that simply typing in “nanotechnology” or “nanomaterials with emissions reductions” brought up thousands of journal articles not relevant to the subject matter of this report. After a series of keyword shuffles, the CTR library staff narrowed down key words, arriving at a list of 400+ articles. Some 200 were downloaded, read, and reviewed, and approximately 70 are discussed in this report. What is clear is that much R&D needs to be conducted to determine how nano TiO2 can be utilized at a commercial scale on concrete and asphalt pavements. While considerable research has been conducted, and this product is commercially available, it is neither cheap nor ubiquitously used. Research being conducted right now is still discovering the multitude of combinations, properties, longevity, and durability of different application methods of this product in a laboratory setting and in small field trials.

As in many new disruptive technologies, there is still some hype over the benefits of nanomaterials and products. One study noted “*Results showed that increasing load cycles, photocatalytic activity of sprayed material is reduced up to half of the initial value”* and the Government Accountability Office (GAO) has stated that *“The extent to which nanomaterials present a risk to human health and the environment depends on a combination of the toxicity of specific nanomaterials and the route and level of exposure to these materials. Although the body of research related to nanomaterials is growing, the current understanding of the risks posed by these materials is limited”* (GAO, 2010). The GAO also noted that the Environmental Protection Agency *“faces challenges in effectively regulating nanomaterials that may be released in air, water, and waste because it lacks the technology to monitor and characterize these materials or the statutes include volume based regulatory thresholds that may be too high for effectively regulating the production and disposal of nanomaterials”* (GAO, 2010).

Notwithstanding these cautionary components, the research reviewed revealed significant promise in the ability of just one nano product—nano titanium dioxide—to reduce multiple types of pollutants at a significant level, sometimes up to 60 to 70%, on both concrete and asphalt pavements and in barriers and sound walls. Figure 1.1 shows nitric oxide removal efficiency using $TiO_2$.




*Source: Leng et al., 2018*

*Figure 1.1 Nitric Oxide Removal Efficiency Results*

Doubtless, as technologies improve and become cheaper, opportunities will arise to enable use of such materials, even after infrastructure is built.

Areas of further research into the use of nanomaterials for storm water and water runoff also show some promise, as current research is looking at nanotechnology to break down and biodegrade components within sewage and waste water.

Finally, other areas that may also provide impetus for cross-pollination of research for transportation infrastructure may also come out of the Department of Energy and the Department of Defense's large R&D budget allocations for nanotechnology.

# Chapter 2. Nanotechnology: An Introduction

This chapter will cover three main topic areas:

1. Introduction and overview to nanotechnology
2. The federal role and current investment
3. National level research, initiatives, and organizations

## 2.1. Overview of Nanotechnology Science

As noted, nanotechnology science is expected to deliver societal and economic benefits in multiple fields.

Nanotechnology operates at the scale of 1 to 100 nanometers (one nanometer = billionth of a meter). Nanoscale occurs naturally in nature. For example, hemoglobin is 5.5 nanometers in diameter, one strand of DNA is 2 nanometers in diameter, and a human hair is 80,000 nanometers in diameter. Properties of matter at this size are fundamentally different than the properties of individual atoms and molecules. According to the National Nanotechnology Initiative (NNI),

> "when particles are created with dimensions of about 1–100 nanometers (where the particles can be "seen" only with powerful specialized microscopes), the materials' properties change significantly from those at larger scales. This is the size scale where so-called quantum effects rule the behavior and properties of particles. Properties of materials are size-dependent in this scale range. Thus, when particle size is made to be nanoscale, properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle."

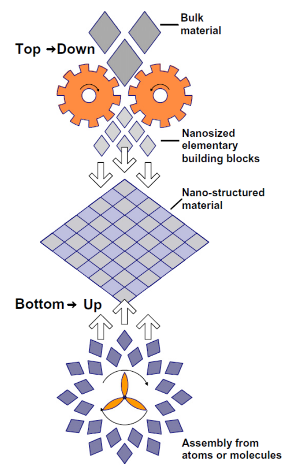
As a consequence of these properties, nanoscale materials have far larger surface areas than similar masses of larger-scale materials. This means that as surface area per mass of a material increases at the nanoscale, a greater amount of the nanoscale material can come into contact with surrounding materials, thus affecting reactivity. In the case of titanium dioxide ($TiO_2$) applied to concrete to create photocatalytic concrete, this greater surface area allows the remediation of $CO_2$ and $NO_x$ and other chemicals when the surface is exposed to ultraviolet (UV) rays from sunlight. When rain (or water that is applied) reacts with the $TiO_2$ and UV light, it undergoes a chemical change and allows the pollutants to, in essence, wash away.

In a 2012 report the GAO noted that:

> "Nanomaterials come in a variety of forms based both on their chemical composition and physical structure. For example, carbon-based nanomaterials can be produced in a number of physical structures such as sheets (graphene), tubes (carbon nanotubes), and particles (carbon black). Nanomaterials can enter the marketplace as materials themselves, as

intermediates that either have nanoscale features or incorporate nanomaterials, and as final nano-enabled products" (GAO 12-427, 2012).

Nanotechnology is derived from two main approaches according to Sanchez and Sobolev (2010). Firstly, in the ‘‘top-down" approach, larger structures are reduced in size to the nanoscale but maintain their original properties without atomic-level control (for example, electronics miniaturization) or are deconstructed from larger structures into their smaller, composite parts. Secondly, in the ‘‘bottom-up" approach (also called "molecular nanotechnology" or ‘‘molecular manufacturing"), materials are engineered from atoms or molecular components through a process of assembly/self-assembly (Sanchez and Sobolev, 2010). Figure 2.1 shows the two processes.




*Source: Sanchez and Sobolev, 2010*

*Figure 2.1 The Top-Down and Bottom-Up Approaches in Nanotechnology*

Nano material types fall into four main categories (GAO 10-549, 2010).

"Carbon-based materials. These nanomaterials are composed mostly of carbon, and are most commonly spherical, elliptical, or tubular in shape. Spherical and elliptical carbon shapes are referred to as fullerenes, while tubular ones are called nanotubes.

Metal-based materials. These nanomaterials include nanoscale gold, nanoscale silver, and metal oxides, such as TiO2. They also include quantum dots, which are closely packed semiconductor crystals comprised of hundreds or thousands of atoms, on the scale of a few nanometers to a few hundred nanometers.

Dendrimers. These nanomaterials are nanoscale polymers built from branched units. The surface of a dendrimer has numerous branch ends, which can be tailored to perform specific chemical functions. Also, some dendrimers contain interior cavities into which other molecules can be placed, such as for drug delivery.

Composites. These materials combine nanoparticles with other nanoparticles or with larger, conventional-scale materials. For example, nanoparticles, such as nanoscale clay

> can be combined with other materials to form a composite material" (GAO 10-54p, 2010 pp 6).

Much of the current technology developments and applications are incremental—some say evolutionary—in nature, offering what seem like very modest improvements. The major areas where nanotechnology is playing a current substantive fundamental role is in microchips, and storage density of memory in computing. Consumer products that incorporate nanotechnology are currently found in the areas of clothing, cosmetics, household appliances, and sporting goods (GAO, 2012). A 2010 study by Roco et al. estimated that products enabled by nanotechnology would double every 3 years globally with an estimated $3 trillion market and 6 million workers by 2020 (Roco et al., 2010). *Azonano* magazine estimates the global market for nanotechnology will exceed $124 billion by 2024 (Cuffari, 2018).

Over the longer term, nanotechnology is anticipated to deliver major advances that may have profound implications for society as well benefits in the areas of:

- Detection and treatment of disease
- Renewable energy
- Water treatment
- Environmental remediation
- Emission reduction
- Agricultural and food applications
- Self-healing materials
- Toxin and pathogen sensors

Notwithstanding the excitement over the potential for nanotechnology to enhance and augment current processes, potential risks are expected to arise from exposure to nanomaterials during manufacture use and end-of-life disposal. The GAO noted:

> "The use of nanomaterials in commercial applications raises questions about the potential risks that might arise from exposures to nanomaterials and the differences in exposure during their manufacture, use, and disposal. For example, some, but not all, research studies have shown adverse respiratory or cellular effects in animals exposed to some types of carbon nanotubes. Observed effects include early onset and persistence of pulmonary fibrosis and interference with cell division. The risk posed by a material is a combination of the hazard or negative effect that material may have on an organism and the extent of the organism's exposure to that material. Therefore, a highly poisonous material—that is, one with high hazard—may nonetheless pose little risk if susceptible groups have little or

no contact with the material. For instance, many household chemicals are hazardous to human health but pose little risk when exposure is limited by safe handling. Conversely, a material with relatively mild health effects may pose a large risk if people or the environment are exposed to large amounts or over prolonged periods" (GAO 12-427, 2012).

## 2.2. Federal Role and Investment

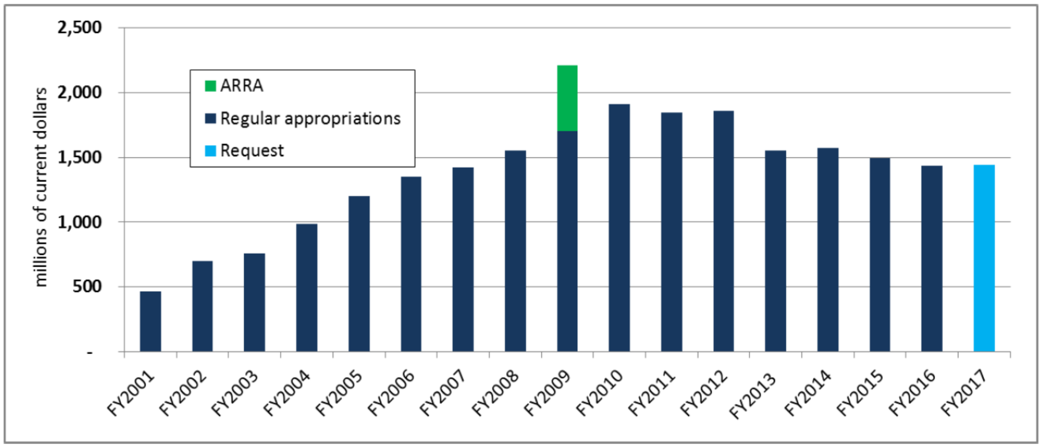
The United States Congress began supporting R&D in 2000. Nanotechnology research has been directed to three major topic areas: federal R&D investments, U.S. international competitiveness and environment, and health and safety concerns.

Funding began in 2001 when the U.S. Congress appropriated just under $500 million dollars for agencies conducting nanotechnology work. This rose to $1.5 billion by 2017 (Figure 2.2). The President's 2018 budget provided for $1.2 billion in support to the NNI.

In 2003 the U.S. Congress passed the 21st Century Nanotechnology Research and Development Act of 2003 (Public Law 108-153, 15 USC §7501). The law authorized the legislative foundation for the NNI, established programs, and assigned agency responsibilities, along with setting funding approval levels for various federal agencies. The law, however, had some provisions that had expiration dates that have already passed. Attempts to develop comprehensive reauthorization of the act took place during the 110th through 114th Congress. These were unsuccessful. For example, during the 114th Congress, H.R. 1898 Subtitle B of the America Competes Reauthorization Act of 2015 (H.R. 1898) would have reauthorized the NNI; and The American Innovation and Competitiveness Act (S. 3084) would have modified certain NNI statutory reporting requirements. No bills have been introduced during in the 115th and the current 116th Congress.

According to the Congressional Research Service (CRS), the U.S. is estimated to account for approximately a third of total global nanotechnology R&D (CRS, 2016). Three federal agencies conduct nanotechnology R&D but also have regulatory responsibilities: the Environmental Protection Agency (EPA), Food and Drug Administration, and Consumer Product Safety Commission.

**Figure 1. NNI Funding in Current Dollars, FY2001-FY2017**

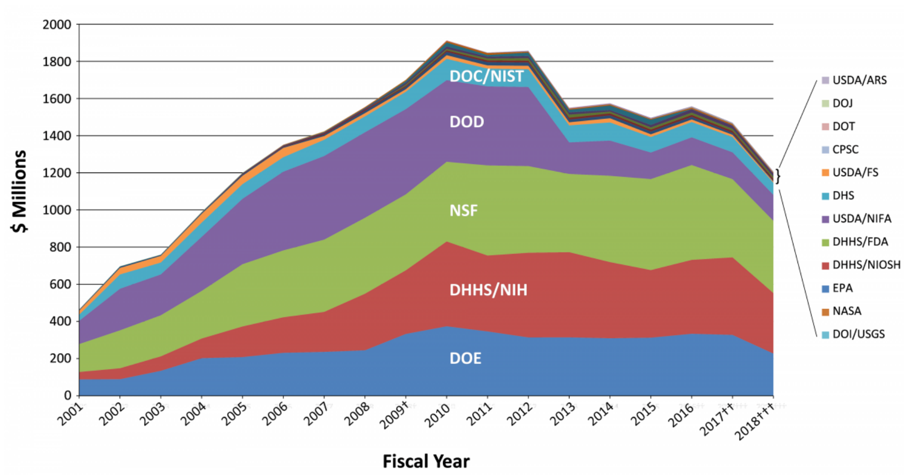



**Source:** CRS analysis of NNI data.

*Source: CRS, 2016*

*Figure 2.2 NNI Funding in Current Dollars, FY2001–2017*

Figure 2.3 depicts the split of funds by agencies since 2001. The U.S. Department of Transportation (USDOT) slice of this pie is very small compared to other agencies.




*Source: NNI Website, not dated*

*Figure 2.3 Agency Allocations from NNI Budget Appropriations*

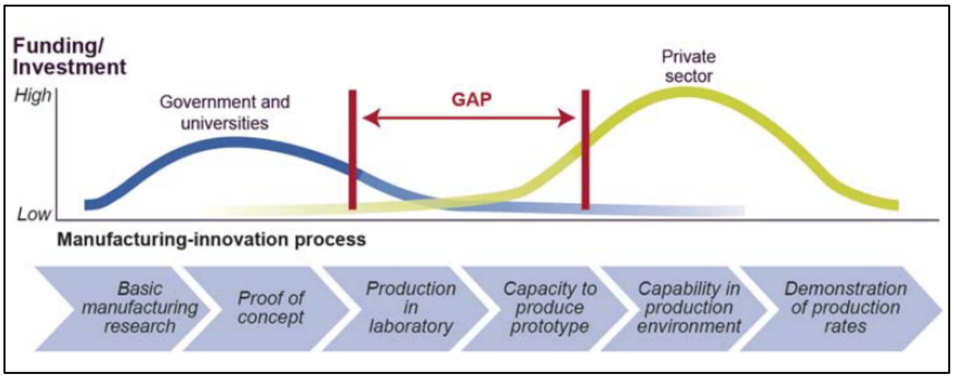
The GAO in 2013 reported on a forum that was convened by the Comptroller General of the United States (GAO 14-181SP, 2014). This report noted two major funding and investments gaps, termed the "Valley of Death" and the "Missing Middle," which had been identified by the President's Council of Advisors on Science and Technology (PCAST) in July 2012.

The GAO definitions for these are the following:

> "*The Valley of Death* refers to a gap in funding or investment that can occur after research on a new technology and its initial development—for example, when the technology moves beyond tests in a controlled laboratory setting. The term *Missing Middle* has been used to refer to the lack of funding/investment that can occur with respect to manufacturing

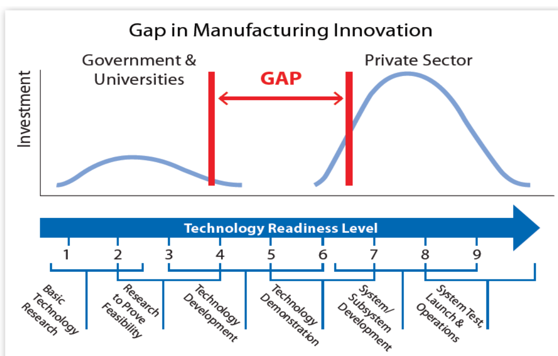
innovation—that is, maturing manufacturing capabilities and processes to produce technologies at scale innovation—that is, maturing manufacturing capabilities and processes to produce technologies at scale. Here, another important lack of support may be the absence of what one participant called an "industrial commons" to sustain innovation within a manufacturing sector. Logically, successful transitioning across the middle stages of manufacturing development is a prerequisite to achieving successful new approaches to manufacturing at scale." (GAO, 14-181SP, 2014 pp 25-26),

Figure 2.4 shows where these gaps occur (GAO, 2014) and Figure 2.5 shows the original figure developed by PCAST.




*Source: GAO, 14-181SP, 2014*

*Figure 2.4 Funding Investment Gap in the Manufacturing-Innovation Process*




*Source: PCAST, 2012*

*Figure 2.5 Manufacturing Innovation: Investment Gap*

The GAO issued further reports in 2014 on nanomanufacturing, including one on nanomanufacturing and U.S. competitiveness in which testimony was given before the Subcommittee on Research and Technology; Committee on Science, Space, and Technology; U.S. House of Representatives (GAO, 14-618, 2014). This report noted that nano-based concrete was being heavily used, and that the U.S. had a 15% market share of chemical sales worldwide. The testimony noted, however, that:

> "Experts offered differing views on U.S. global competitiveness in the commercialization and use of nanomaterials in concrete. A key forum participant said that while cement for domestic use is produced in the United States, today's dominant companies—which are spearheading development of new technologies—are headquartered elsewhere (although this industry was previously dominated by the United States). Additionally, some experts said that other countries are spending more resources than the United States to promote commercialization; for example, one expert said that China established a national technology center to improve its competitiveness and domestic production of high-value, nano-based construction products" (GAO 14-618, 2014 pp6).

## 2.3. National Research Initiatives and Organizations

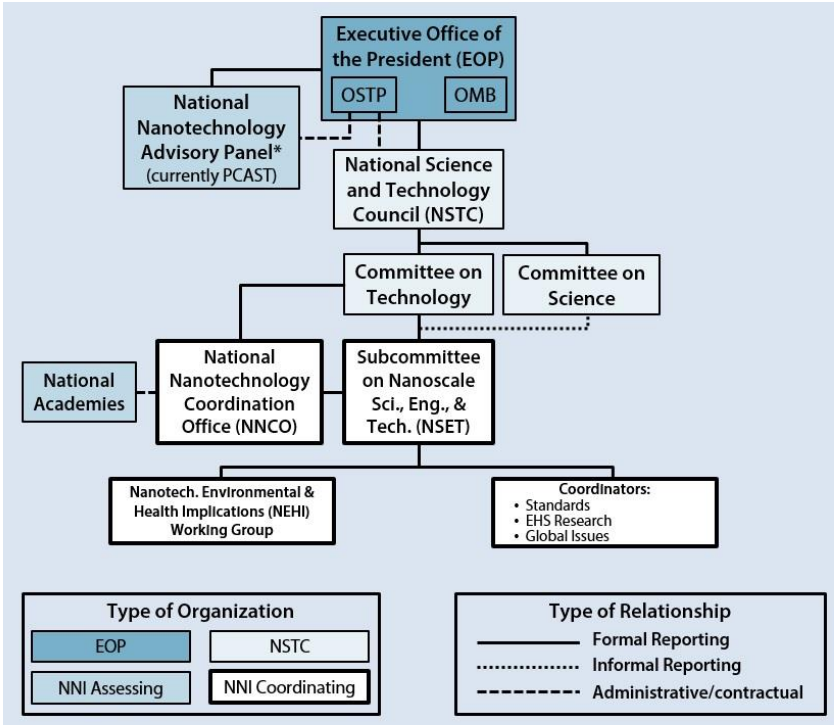
### 2.3.1. The National Nanotechnology Initiative

In 2000 President Clinton launched the NNI to coordinate all federal R&D activities and to promote U.S. competitiveness in this area. However, as noted above, overall federal funding has declined from a zenith in 2010, coupled with the lack of reauthorization of the 21st Century Nanotechnology Research and Development Act. While no specific funds were authorized as a consequence of the lack of reauthorization, Congress has continued to support the NNI with annual appropriations. The executive branch has also operated and reported on the NNI annually.

The NNI is coordinated within the White House through the National Science and Technology (NSET) Council subcommittee. The NSET subcommittee has 20 representatives from federal departments and agencies, the Office of Science and Technology Policy, and the Office of Management and Budget (OMB). The NSET subcommittee has two working groups: National Environmental and Health Implications, and Nanotechnology Innovation and Commercialization Ecosystem. Two previous working groups were eliminated (Global Issues in Nanotechnology and Nanotechnology Public Engagement and Communications). Figure 2.6 shows the NNI structure.

The NNI reports their research funding by area to the OMB as part of the annual budget process, although it should be noted that they do not report on project level data to the OMB.

The NNI has developed numerous strategic plans to identify categories of investments that are termed *Program Component Areas* (PCA). This provides a way to inform Congress and the executive branch on investments by area. The PCAs also cross-cut across individual agencies to aggregate up across thematic areas. The five current PCAs are Nanotechnology Signature Initiatives; Foundational Research; Nanotechnology-enabled Applications, Devices, and Systems; Research Infrastructure and Instrumentation; and Environment, Health, and Safety.




*Source: NNI Website, not dated*

*Figure 2.6 Structure of NNI*

Within the Nanotechnology Signature Initiatives PCA, dedicated funds are allocated for these specific and targeted focus areas:

- nanotechnology for solar energy collection and conversion
- sustainable nanomanufacturing
- nanoelectronics for 2020 and beyond
- nanotechnology knowledge infrastructure
- nanotechnology for sensor and sensors for nanotechnology

Transportation could take advantage of such dedicated funding across four of these areas currently, and nanoelectronics may be an area that will serve transportation in the future within automated and connected infrastructure and vehicles.

# Chapter 3. Nanotechnology in Transportation Infrastructure

This chapter will cover these three topic areas:

1. Discussion on literature review methodology and approach.
2. Current R&D in nanotechnology use to achieve emissions reductions in transportation infrastructure.
3. The hype around nanotechnology.

## 3.1. Literature Review Approach and Methodology

A literature search was conducted using multiple database sites, with a time span back to 2000. This was done in an effort to reduce sources that were not relevant. The goal in this search was to find material that was pertinent and relevant. As explained in Chapter 1, simply typing in "nanotechnology" or "nanotechnology and emissions" returns an overwhelming number of results, not all of which are relevant. Keywords used included the following:

- Nanoparticle, air quality
- Nanotechnology and emission
- Nanotechnology, emission, and air quality
- Nanoparticle
- Concrete
- Reducing carbon emission with nanoparticles
- Reducing carbon emission with nanotechnology
- Nanoparticle + emission reduction + building + wrap
- Nanotechnology + emissions reduction
- Nanotechnology Co2 capture
- Nanotechnology climate change
- Nanomaterials could combat climate change and reduce pollution

Google Scholar searches were also conducted with these keywords:

- Building coatings to reduce emissions
- Building coating + emissions reduction

TxDOT noted at the outset of this literature review search request that at the Transportation Research Board's (TRB) Annual Meeting sessions were held on pavements and the urban climate (Session 1111), and decarbonizing transportation: advanced emissions controls (Session 1252). However, the online database from the annual meeting did not make available any PowerPoints or papers to review for these two sessions.

During the search period, CTR also reviewed the websites of the U.S. government, European Union, and other international groups and non-government organizations. The websites visited are listed in Table 3.1.

**Table 3.1 Websites Visited**

| Entity | Type | URL |
|---|---|---|
| Whitehouse.gov | Office of President | https://www.whitehouse.gov/wp-content/uploads/2018/08/The-National-Nanotechnology-Initiative-Supplement-to-the-President%E2%80%99s-2019-Budget.pdf |
| National Nanotechnology Initiative | National U.S. federal organization. | https://www.nano.gov/ |
| The National Academies | National Organization | http://www8.nationalacademies.org/onpinews/newsitem.aspx?RecordID=10395 |
| United States Forest Service: R&D Nanotechnology | Federal Agency | https://www.fs.fed.us/research/nanotechnology/ |
| US EPA | Federal Agency | https://www.epa.gov/sites/production/files/2015-01/documents/nanotechnology_whitepaper.pdf |
| CDC | Federal Agency | https://www.cdc.gov/niosh/topics/nanotech/faq.html |
| Virginia DOT | State DOT Nanotechnology of Concrete – conference | https://www.virginiadot.org/VDOT/Business/asset_upload_file772_3638.pdf |
| American Museum of Natural History | Education | https://www.amnh.org/learn-teach/curriculum-collections/young-naturalist-awards/winning-essays/2008/investigating-the-effect-of-silver-nanoparticles-on-aquatic-organisms |
| European Union | International Trading Block | http://ec.europa.eu/environment/integration/research/newsalert/pdf/75na3_en.pdf |
| World Economic Forum | International Organization | https://www.weforum.org/agenda/2015/07/5-ways-nanotechnology-can-tackle-climate-change/ |
| OECD | International Organization | https://www.oecd-ilibrary.org/docserver/5k450q9j8p8q- |

| Entity | Type | URL |
| --- | --- | --- |
| | | en.pdf?expires=1563306945&id=id&accname=guest&checksum=6302979E613CAC04086CF4F3BCF70DD1<br><br>http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=DSTI/STP/NANO(2012)14&docLanguage=En<br><br>https://www.oecd.org/science/nanosafety/44108334.pdf |
| ASEE | NGO | http://www.asee.org/documents/sections/2012/Midwest/ASEE_Midwest_2012_Asmatulu_Effects_of.pdf |
| AIP 2018 Nano Innovation 2017 Conference Proceedings | Conference proceedings | https://aip.scitation.org/doi/pdf/10.1063/1.5047755 |
| Azo Nano | Online journal | https://www.azonano.com/aboutus.aspx |
| Science Daily | Journal/newsfeed | https://www.sciencedaily.com/releases/2018/09/180927145555.htm |
| Nano Werk | Journal/Aggregator | https://www.nanowerk.com/ |
| Center for Sustainable Nanotechnology | Institute | http://sustainable-nano.com/2016/02/02/nanotechnology-and-climate-change-finding-connections/ |
| Institute of Development Studies | Institute | https://www.eldis.org/document/A42819 |
| Foresight Institute | NGO | https://foresight.org/nanotechnology-vs-climate-change/ |
| Electronic Privacy Information Center | NGO | https://epic.org/privacy/nano/ |
| Sustainable Buildings initiative | NGO | https://sustainablebuildingsinitiative.org/toolkits/emissions-reduction-toolkits/energy-efficiency/office-design/?toolkit=97 |
| Friends of the Earth | NGO | https://friendsoftheearth.uk/sites/default/files/downloads/nanotechnology_climate.pdf |
| IPEN | NGO | http://www.wecf.eu/download/2009/FINAL-OECDenvironmentalBrief130709.pdf |

## 3.2. Overview of Current Topics of Nanotechnology R&D in Transportation Infrastructure

The literature search revealed that while there is significant research in nanotechnology, narrowing this area down to transportation infrastructure specifically, and then to emissions reduction as a singular topic, reduced the number of pertinent items. The 2009 Nanotechnology in Construction Conference proceeding output (published in book form) noted that the construction industry is not as dynamic as other industries, and that size and scale played a role (Nanotechnology in Construction, 2009). Tables A1 and A2 in the appendix list all the papers reviewed for this analysis.

The literature searches revealed significant research in the use of nanotechnology for tailpipe emission reduction, power plant emission remediation, indoor air conditioning filters that used nanotubes to capture multiple types of toxic compounds and gases, and the use of nanotechnology for water purification and for renewable energy—specifically in the coatings for solar panels and in the use of nanotechnology for greater conductivity in electric parts of solar arrays.

What was clear in the literature is that $TiO_2$ has been studied for over twenty years for its ability to reduce emissions when used in concrete and in asphalt. There was very little else in the literature regarding emission reduction using nano technology in transportation, aside from the expected plethora of research looking at emission reduction within the catalytic converter of an engine.

Haghighat et al. (Haghighat et al., 2019) reviewed the hydrothermal/solvothermal synthesis (HST) and treatment of for photocatalytic oxidation (PCO) of air pollutants, specifically focusing on the preparation, characterization, properties, and performance of $TiO_2$ for air purification. This critical review of HST for noted that:

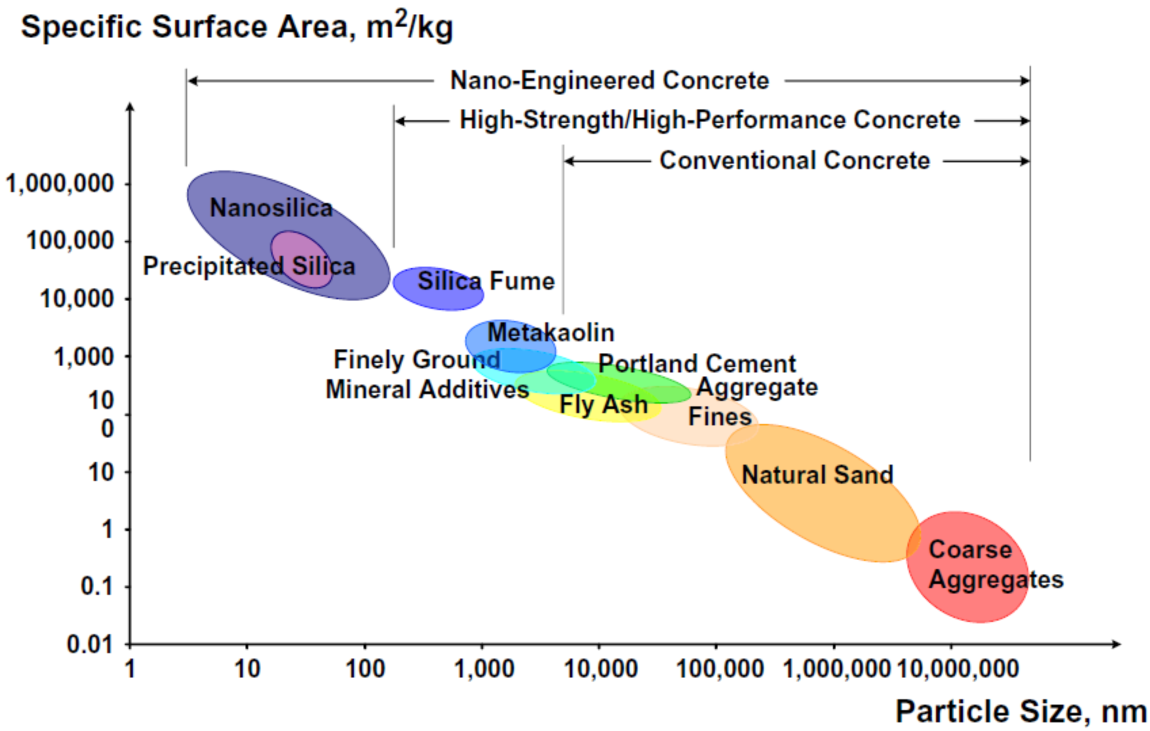
> "In order to advance PCO acceptability into large-scale application in air purification, it is crucial to develop more efficient and durable photocatalysts. Hence, synthetic methods with better control over physical and chemical characteristics of $TiO_2$ are of great importance. In this regard, hydrothermal/solvothermal technique has shown great promises by overcoming some of the most critical shortcomings of photocatalysts derived from other methods."

Sanchez and Sobolev (Sanchez and Sobolev, 2010) give an excellent definition of nanotechnology and concrete. Table 3.2 provides their definitions.

**Table 3.2 Definitions of Concrete and Nanotechnology in Concrete**

| **Concrete: a complex, nano-structured material** | **Definition of nanotechnology in concrete** |
|---|---|
| "Concrete, the most ubiquitous material in the world, is a nanostructured, multi-phase, composite material that ages over time. It is composed of an amorphous phase, nanometer to micrometer size crystals, and bound water. The properties of concrete exist in, and the degradation mechanisms occur across, multiple length scales (nano to micro to macro) where the properties of each scale derive from those of the next smaller scale. The amorphous phase, calcium–silicate–hydrate (C–S–H) is the ''glue" that holds concrete together and is itself a nanomaterial. Viewed from the bottom-up, concrete at the nanoscale is a composite of molecular assemblages, surfaces (aggregates, fibers), and chemical bonds that interact through local chemical reactions, intermolecular forces, and intraphase diffusion. Properties characterizing this scale are molecular structure; surface functional groups; and bond length, strength (energy), and density. The structure of the amorphous and crystalline phases and of the interphase boundaries originates from this scale. The properties and processes at the nanoscale define the interactions that occur between particles and phases at the microscale and the effects of working loads and the surrounding environment at the macroscale. Processes occurring at the nanoscale ultimately affect the engineering properties and performance of the bulk material." | "The nanoscience and nano-engineering, sometimes called nanomodification, of concrete are terms that have come into common usage and describe two main avenues of application of nanotechnology in concrete research... *Nanoscience* deals with the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this structure affects macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. *Nano-engineering* encompasses the techniques of manipulation of the structure at the nanometer scale to develop a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks. Concrete can be nano-engineered by the incorporation of nanosized building blocks or objects (e.g., nanoparticles and nanotubes) to control material behavior and add novel properties, or by the grafting of molecules onto cement particles, cement phases, aggregates, and additives (including nanosized additives) to provide surface functionality, which can be adjusted to promote specific interfacial interactions." |

Figure 3.1 shows the particle size and specific surface area related to concrete materials.




*Source: Sanchez and Sobolev, 2010 pp 2065*

*Figure 3.1 Particle Size and Specific Surface Area Related to Concrete Materials*

The next section takes provides a chronological review of the literature (2001 through 2019).

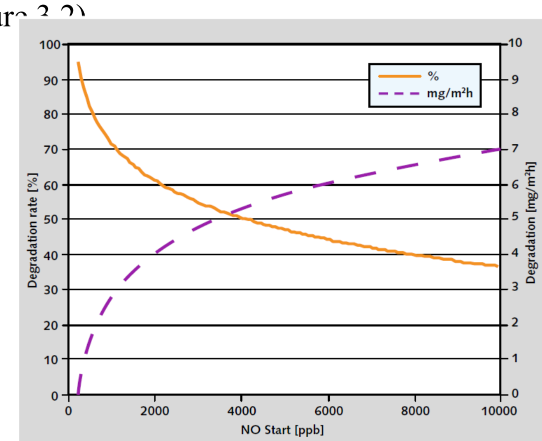
In 2001, Nakamura and Meiarashi looked at $NO_x$ removal using carbonized aggregate that was coated with $TiO_2$. They found that the $NO_x$ removal capability was very high and could become a material for air pollution emission reduction (Nakamura and Meirashi, 2001). In their experiment they used a woody material (medium density fiberboard) of 15mm thickness that was processed to create globular woodchips. This was then coated with $TiO_2$ by soaking for five minutes; the fiberboard was then placed into a centrifuge to remove excess. This was then placed into a reactor vessel, and the composite was irradiated with UV rays using a black light, as test gas was introduced. $NO_x$ concentration was measured for thirty minutes as the UV radiation finished. Using an electron microscope, the area coated with $TiO_2$ showed a change in surface area and the results showed that $NO_x$ removal ratio was as high as 60%.

In 2008 Poon and Cheung looked at photocatalytic paving blocks (again coated with $TiO_2$ made from local waste materials—construction/demolition waste and waste glass cullet). These were then field trialed and monitored. They found that $NO_x$ concentration was reduced approximately 13% at ground level and 10% at human height level (Poon and Cheung, 2007).

Guang et al., in 2008, developed a test chamber with 2, 3, 4, and 5% of nano TiO2 photocatalytic materials that were mixed with high shear ultrasonic wave and dispersant to look at the degradation of $NO_x$, hydrocarbons (HC), and carbon monoxide (CO) from a tailpipe when vehicle was idle

(Guang, 2008). The test results were that "*Nano titanium dioxide made by ultrasonic dispersant has the best degradation efficiency on $NO_x$ of automotive emission. The nano titanium dioxide made by high shear, ultrasonic wave and ultrasonic dispersant, degrading of NOx, HC, CO on automotive emission is 5%, 3%, 2%; 5%,3%,4%; 5%, 2%, 3% respectively*" (Guang et al., 2008).

Bolte in 2009 looked at applications of the trademarked TioCem® used on roof tiles and cement blocks within a test chamber to measure exposure with and without light. This study found significant degradation of pollutants even at intensities "well-below those described in various measuring methods" (Figure 3.2).




4 Degradation rates as a function of initial NO content on concrete paving; air flow-rate 1 l/min.; UV-A intensity 2000 μW/cm²

*Source: Bolte, 2009*

*Figure 3.2 Degradation Rates as a Function of NO Content on Concrete Paving*

Sanchez and Sobolev in their 2010 review of nanotechnology in concrete noted that nano $TiO_2$ had been proven effective for self-cleaning of concrete, as well as the added benefit of reducing emissions, although there was some aging due to carbonation that could result in catalytic efficiency loss. Nano-$SIO_2$ [silicon dioxide] has also been found to improve concrete workability and strength and an increased resistance to water penetration, and had accelerated the hydration reactions of $C_3S$ and ash-cement mortar and showed enhanced strength than silica fume. Many of these results were, however, highly dependent on the production route, conditions of the Nano-$SIO_2$ and the types of reagents and duration of the reaction in the sol-gel method. Nano-$Fe_2O_3$, they also noted, had been found to provide concrete with self-sensing capabilities as improved its compressive and flexural strengths (Sanchez and Sobolev, 2010).

Hassan et al. reviewed a nano-TiO2 additive on asphalt binder aging properties in 2011. This study was undertaken as the technology was only being applied to concrete pavement surfaces, which represented about 6% of the national road network in the U.S. (Hassan et al., 2011). Asphalt, meanwhile, is used in approximately 94% of the U.S. road network (primarily hot-mix asphalt), and they thus considered that research was needed to developing a method for using $TiO_2$ coating in flexible pavements. They used a commercial crystallized anatase-based $TiO_2$ powder that was blended with a conventional asphalt binder (classified at PG64-16 at three modification rates 3%, 5% and 7% respectively). They found:

"Prepared blends were characterized with the use of fundamental rheological tests and with measurements of the environmental efficiency of the binder in removing part of the $NO_x$ pollutants from the airstream. Results of the experimental program indicated that the use of$TiO_2$ as a modifier to asphalt binder was effective in removing part of the $NO_x$ pollutants from the air stream. Rheological test results indicated that the addition of $TiO_2$ did not affect the physical properties of the conventional binder. Exposing the binder to ultraviolet light did not appear to accelerate the aging mechanisms in the binder" (Hassan et al., 2011).

Shen et al. studied the effectiveness of treated pervious concrete by comparing different $TiO_2$ application methods (Shen et al., 2012). At the time of testing they noted that there was very little commercial availability of photocatalytic building materials, and the average cost of ultrafine nano $TiO_2$ was $9.07 per pound. They also tested the durability under freeze-thaw conditions with a de-icing agency and outside weathering. The batches of trial samples used six different $TiO_2$ coating methods and different concentrations in each.

1. **Cement/aggregate mix (CAM):** it was a thin layer of pervious concrete with finer aggregate size and $TiO_2$ mixed in. This could be used as a special application when surface maintenance is needed for pervious concrete.
2. **Driveway protector mix (DPM):** it consisted of a transparent liquid driveway protector and $TiO_2$ uniformly mixed together and brushed onto the surface of pervious concrete.
3. **Cement-water slurry high (CWSH):** it consisted of a relatively high concentration of cement and $TiO_2$ mixed into water and brushed onto the surface of pervious concrete.
4. **$TiO_2$ sprinkled on driveway protector (SDP):** it consisted of $TiO_2$ sprinkled onto driveway protector freshly painted on the surface of pervious concrete.
5. **$TiO_2$ sprinkled on fresh concrete (SFC):** it consisted of $TiO_2$ sprinkled onto fresh pervious concrete.
6. **$TiO_2$ mixed in water on fresh concrete (TIWF):** it consisted of $TiO_2$ sprinkled onto fresh pervious concrete (Shen et al., 2012)

Plain pervious concrete samples with no $TiO_2$ were also tested, as they were used as control specimens (Shen et al., 2012). Their analysis and testing found:

"High pollutant reductions were seen with a driveway protector mix, a commercial water-based $TiO_2$ preparation, $TiO_2$ in water, a cement-water slurry with low cement concentration, and the commercial PURETI coating. It was found that nitrogen oxide (NO) was efficiently removed with each of these treatments, while VOCs displayed more variability in removal efficiency. When pervious concrete was compared to traditional concrete, pervious concrete showed higher NO reductions. The PURETI coating had the lowest effect on reducing the infiltration rate of the pervious concrete. The driveway protector mix had the highest resistance against freeze-thaw testing with deicing chemical and environmental weathering. From Scanning Electron Microscopy (SEM), $TiO_2$ appeared to be more abundant and evenly distributed over the surface of the driveway protector mix. Based on the findings from this study, it is recommended that each coating type be applied for different purposes. For example, the driveway protector mix would resist well in a highly abrasive environment, like on the shoulders of a highway or on busy sidewalks adjacent to a road. The transparent color of the commercial water-based $TiO_2$ could be used for aesthetic reasons. The cement aggregate mixes could be mixed into thin pervious concrete overlay, as a pavement maintenance technique. The PURETI treatment as a cost-effective alternative, where the surface abrasion is low. More studies need to be done to confirm each treatment's resistance against live traffic and against weathering during the colder and wetter seasons" (Shen et al., 2012).

At the American Society of Civil Engineers (ASCE) Transportation and Development Institute Congress in 2011, Schmitt et al. (Schmitt et al., 2011) presented "Impact of Mixed Nitrogen Dioxide (NO/d2) and Nitrogen Oxide (NO) Gases on Titanium Dioxide Photodegradation of NO/dx." This study evaluated the environmental effectiveness of $TiO_2$ coating in photodegrading mixed $NO_2$ and NO gases from the atmosphere. Their results indicated that *"Results of the experimental program determined that increasing the flow rate and $NO_2/NO_x$ ratio negatively affect the effectiveness of the photocatalytic process. However, within the evaluated range, the titanium content and aggregate gradation had little impact on $NO_x$ removal efficiency. The highest photo degradation rate was observed at 25% relative humidity, which balances the availability of hydroxyl radicals at the surface with $NO_x$ contact with the photocatalytic surface"* (Schmitt et al., 2011).

Shen et al. (2012) also looked at the reduction of toluene, trimethylbenzene (TMB), and NO from automobile exhaust. Eight different application mixes were used.

"Commercial water-based $TiO_2$ (CWB): it consisted of Cristal Global's S5-300B commercial water-based $TiO_2$ brushed onto the surface of pervious concrete.

Cement-water slurry high (CWSH): it consisted of cement, water, and $TiO_2$ uniformly mixed together and brushed onto the surface of pervious concrete. The slurry was relatively thick compared to method

Cement-water slurry low (CWSL): it consisted of a thin slurry with low cement concentration and $TiO_2$ uniformly mixed together and brushed onto the surface of pervious concrete.

Driveway protector mix (DPM): it consisted of a transparent liquid driveway protector and $TiO_2$ uniformly mixed together and brushed onto the surface of pervious concrete.

$TiO_2$ in water (TIW): it consisted of water and $TiO_2$ uniformly mixed together and brushed onto the surface of pervious concrete.

PURETI (PUR): it consisted of the PURETI commercial water-based $TiO_2$ applied to the surface with a special electrostatic sprayer by the PURETI producer.

Cement/aggregate mix (CAM): it was a thin layer of pervious concrete with finer aggregate size and $TiO_2$ mixed in. This could be used as a special application when surface maintenance is needed for pervious concrete.

Cement/aggregate mix with higher $TiO_2$ concentration (CAMH): it was the same application method as method but with higher $TiO_2$ concentration." (Shen et al., 2012)

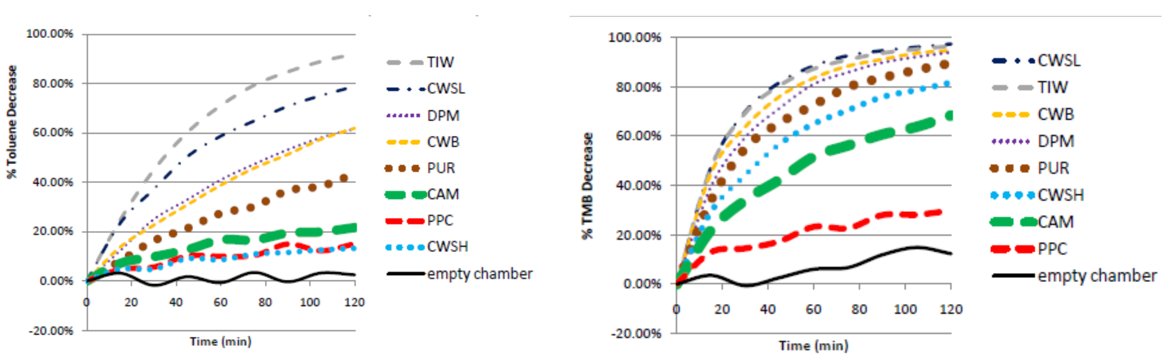
Three control specimens were also tested. Plain pervious concrete with no $TiO_2$ (PPC), plain traditional concrete with no $TiO_2$ (PTC), and traditional concrete coated with the CWSH method (TCC). The results before abrasion are shown in Table 3.3. They also conducted tests for 0, 12- and 36-hour freeze thaw cycles as well. Results of toluene, TMB, and NO reduction can be seen in Figures 3.3 and 3.4.

**Table 3.3 Summary of Results for Each Application Type Before Abrasion**

| Sample | $TiO_2$ ($g/mm^2$) | % of surface coating that is $TiO_2$ | Static Chamber (120 min) total % toluene reduction | Static Chamber (120 min) total % TMB reduction | Flow-through Chamber (29.83 min) Total % NO reduction | NO decay rate, k (1/hr) | Converted Static Chamber (29.83 min) Total % NO reduction | % Decrease in infiltration rate |
|---|---|---|---|---|---|---|---|---|
| empty chamber | - | - | 2.48% | 12.35% | 1.38% | 0.09 | 4.61% | - |
| PPC | - | - | 15.06±0.28% | 29.86±8.83% | 2.51±0.19% | 0.17 | 8.31% | - |
| PTC | - | - | - | - | 1.61% | 0.111 | 5.37% | - |
| TCC | $8.61*10^{-5}$ | 5.01% | - | - | 13.95% | 1.102 | 42.19% | - |
| CWB | $5.27*10^{-4}$ *(water-based $TiO_2$)* | 100% *(water-based $TiO_2$)* | 61.86±14.06% | 94.64±1.85% | 52.46±2.07% | 7.50 | 97.59% | 20.60% |
| CWSH | $8.61*10^{-5}$ | 5.01% | 13.23±1.62% | 81.65±1.50% | 35.97±1.64% | 3.82 | 85.04% | 58.29% |
| CWSL | $8.61*10^{-5}$ | 9.82% | 78.82±9.22% | 97.26±0.63% | 50.79±0.49% | 7.01 | 96.94% | 51.50% |
| DPM | $8.61*10^{-5}$ | 14.29% | 61.65±10.77% | 93.87±1.09% | 53.27±3.63% | 7.79 | 97.92% | 30.49% |
| TIW | $8.61*10^{-5}$ | 11.76% | 91.98±3.08% | 96.34±1.08% | 51.30±2.43% | 7.15 | 97.14% | - |
| PUR | $2.02*10^{-6}$ | - | 43.42±1.79% | 89.50±4.05% | 48.29±3.13% | 6.37 | 95.79% | 11.92% |
| CAM | $8.61*10^{-5}$ | 0.46% | 21.62±4.30% | 68.28±5.99% | 19.11±3.46% | 1.62 | 55.35% | 3.85% |
| CAMH | $2.17*10^{-4}$ | 1.15% | - | - | 32.97±1.73% | 3.34 | 81.03% | -3.49% |

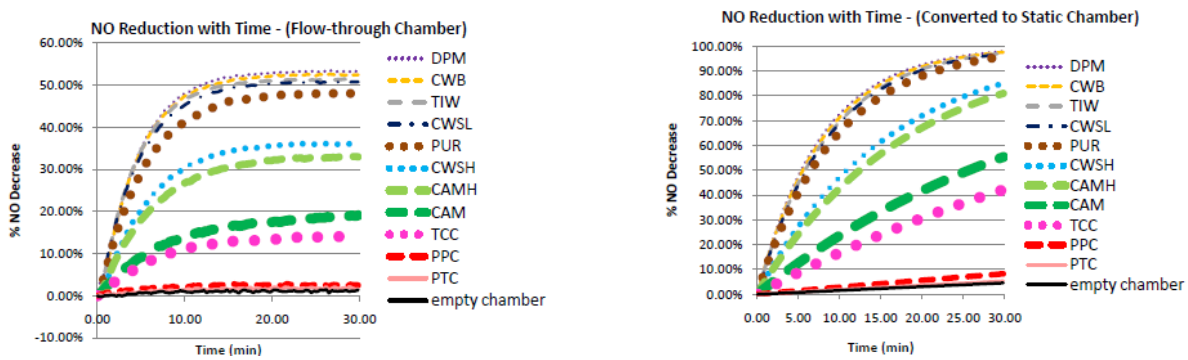
- This data is not applicable or is unavailable.

*Source: Shen et al., 2012*




*Source: Shen et al., 2012*

*Figure 3.3 Results for Static Chamber Reduction in Toluene and TMB after 120 Minutes*




*Source: Shen et al., 2012*

*Figure 3.4 Results for NO Reduction after 30 Minutes with Flow-through Chamber Data and Converted to Static Chamber Data*

They also evaluated materials costs and effectiveness of pollutant reduction (Table 3.4). As the findings indicate, some coating types are more costly and the effectiveness needs to be considered in terms of durability, pollutant reduction, and initial costs.

**Table 3.4 Material Cost & Observed In-Lab Pollutant Reduction for Each Coating Type**

| | MATERIAL COST | | OBSERVED POLLUTANT REDUCTION | | | |
|---|---|---|---|---|---|---|
| | | | Static Chamber (120 min) | | Converted Static Chamber (29.83 min) | |
| **Coating type** | **total material cost ($/ft$^2$)** | **total material cost ($/m$^2$)** | **total % toluene reduction** | **total % TMB reduction** | **Total % NO reduction** | **% Decrease in infiltration rate** |
| commercial water-based $TiO_2$ (CWB) | 0.9955 | 10.70 | 61.86±14.06% | 94.64±1.85% | 97.59% | 20.60% |
| cement-water slurry (CWSH) | 0.1860 | 2.00 | 13.23±1.62% | 81.65±1.50% | 85.04% | 58.29% |
| driveway protector mix (DPM) | 0.3876 | 4.17 | 61.65±10.77% | 93.87±1.09% | 97.92% | 30.49% |
| Pureti (PUR) | 0.1000 | 1.08 | 43.42±1.79% | 89.50±4.05% | 95.79% | 11.92% |
| cement-water slurry low (CWSL) | 0.1655 | 1.78 | 78.82±9.22% | 97.26±0.63% | 96.94% | 51.50% |
| cement/aggregate mix (CAM) | 0.3045 | 3.27 | 21.62±4.30% | 68.28±5.99% | 55.35% | 3.85% |
| cement/aggregate mix high (CAMH) | 0.3030 | 3.26 | - | - | 81.03% | -3.49% |

4 - This data is unavailable

*Source: Shen et al., 2012*

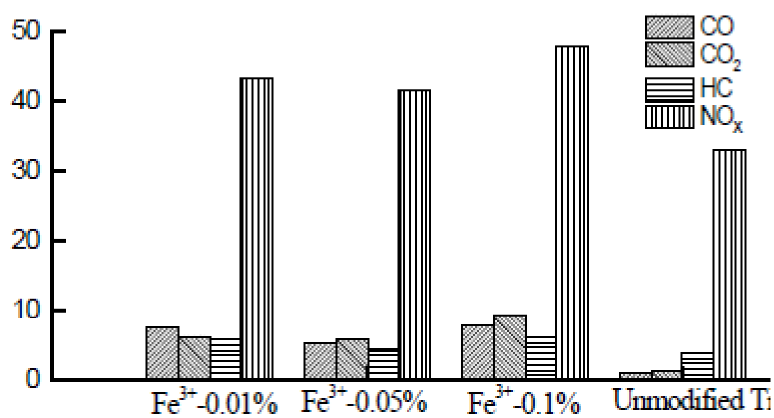
They concluded by noting:

> "Each coating type in this study could be useful for different purposes. For example, because the DPM maintained its high photocatalytic activity after exposure to deicing chemical and freeze-thaw cycles, this type of coating could be used in a highly abrasive environment, like on the shoulders of a highway or on busy sidewalks adjacent to a road. The CWB could be used for aesthetic reasons, where the white color of the DPM is not desired; the CWB is a transparent coating. The white color of the $TiO_2$ particles seen in the DPM coating could potentially be used as pavement marking materials, at the same time achieving air purification effect. The CAM and CAMH coating, $TiO_2$ mixed into thin pervious concrete overlay, could be used as a pavement maintenance technique to address minor surface raveling and cracking distresses at the same time produce photocatalytic

effect. The PUR is a cost-effective light coating, which is suitable for wide low traffic area where the surface abrasion is low."

Meng et al. (Meng et al., 2012) looked at the effect of nano $TiO_2$ on the mechanical properties of cement mortar. In laboratory tests they conducted they when cement was substituted by nano $TiO_2$ they found that the strength of the cement mortar at early stages increased but decreased at later stages. They found that *"The compressive strength of cement mortar with 5% or 10% nano-$TiO_2$ at 1 day both increased by about45%. But the compressive strength of cement mortar at 28 days decreased by 10% and 19% respectively and the fluidity decreased by 20% and 40% respectively when 5% and 10%cement was substituted by nano-$TiO_2$."* They also found that as a consequence of the high surface area of the nano $TiO_2$ they needed more water to enwrap the solid particle.

Pei et al. in 2012 (Pei et al., 2012) assessed the efficacy of using a prepared ferric ion ($Fe^{3+}$) modified $TiO_2$ to reduce emissions in tunnels. In their experiment they saw degradation rate in various catalysts doped with $TiO_2$ that were daubed onto a 300 x 300 mm glass sheet (Figure 3.5) and placed into an exhaust catalytic reaction equipment box they had made.




*Source: Meng et al., 2012*

*Figure 3.5 Degradation rate of CO, $CO_2$, $NO_X$, HC under catalysis of $TiO_2$ doped with respectively 0.1%, 0.05%, 0.01% F3+ and unmodified $TiO_2$*

They concluded that "*Doping $Fe^{3+}$improves photocatalysis performance of nanometer $TiO_2$. The best catalytic effect could be obtained with a $Fe^{3+}$dosage of 0.1%, degradation rates of CO, $CO_2$, HC, $NO_X$ are increased by 6.9%, 7.9%, 2.3%, 14.9% under ultraviolet light conditions; 0.6%, 0.6%, 2.3%, 8.2% under incandescent light conditions*" (Meng et al., 2012, pp 11).

Chen et al. in 2012 (Chen et al., 2012) reviewed the hydration and properties of nano $TiO_2$ blended cement composites. Two different types of nano $TiO_2$ particles were blended into cement pastes and mortars. They found the following:

"The addition of nano-$TiO_2$ powders significantly accelerated the hydration rate and promoted the hydration degree of the cementitious materials at early ages. It was demonstrated that $TiO_2$ was inert and stable during the cement hydration process. The total porosity of the cement pastes decreased and the pore size distribution were also altered. The acceleration of hydration rate and the change of microstructure also affected the physical and mechanical properties of the cement-based materials. The initial and final setting time was shortened and more water was required to maintain a standard consistence due to the addition of thenano-$TiO_2$. The compressive strength of the mortar was enhanced, practically at early ages. It is concluded that the nano-$TiO_2$ acted as a catalyst in the cement hydration reactions" (Chen et al., 2012 pp 648).

Hassan et al. in 2012 (Hassan et al., 2012a) assessed the environmental performance of photocatalytic $TiO_2$ warm-mix asphalt pavements. They noted that the proper method for applying $TiO_2$ to asphalt pavements was unclear, and this study was to evaluate the benefits of incorporating $TiO_2$ in the preparation of warm mix asphalt. They used two types of application methods:

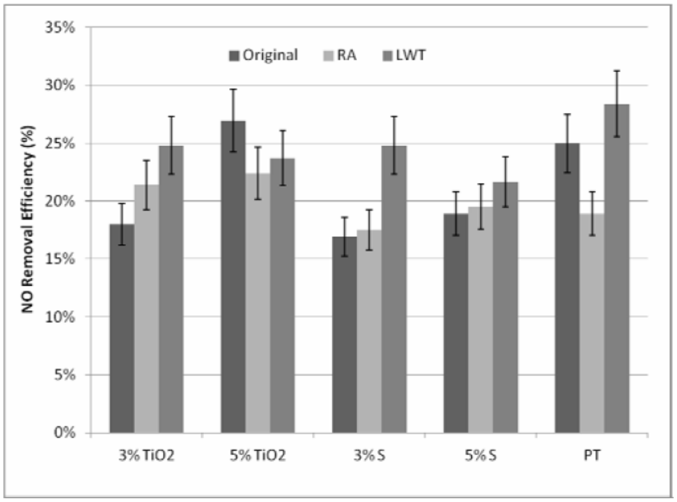
1. Water-based $TiO_2$ solution applied as a thin coating
2. $TiO_2$ added as a modifier to the asphalt binder

They found that the photocatalytic compound, when used as a modifier to the binder, was not effective in degrading $NO_x$ in the air stream. This was attributed to the fact that only a small amount of $TiO_2$ was present at the surface. Conversely the thin coating solution surface spray *"was effective in removing nitrogen oxide ($NO_x$) pollutants from the air stream with an efficiency ranging from 31 to 55%."* The coverage rate that achieved maximum $NO_x$ removal efficiency was of 0:05 L⁄m2. They noted, however, that "*durability of the surface spray coating requires further evaluation."* They also found that the increase in flow rate of air (which included various pollutants) and relative humidity negatively impacted the efficiency and effectiveness of $NO_x$ reduction efficiency. They also found that the increase in UV light intensity improved the $NO_x$ removal efficiency of the surface coating (Hassan, 2012a).

In a different study in 2012, Hassan et al. (Hassan et al., 2012b) reviewed different types of methods to apply $TiO_2$ to concrete pavements. They reviewed three application methods.

1. Cement-based thin coating with a 10mm thickness
2. Water-based TiO2 solution (PT) (2% $TiO_2$ suspended particles and a nano-size 95nm) photocatalytic grade, which gave coverage at a rate of 215 $g/m^2$
3. Sprinkling nano sized TiO2 particles on the fresh concrete surface before hardening. The particles were spread to a content of 3% and 5% after pouring.

The concrete sample dimensions were 305mm x 381mm x 25.4mm. The samples were then subjected to abrasion and wear using accelerated loading test and abrasion, and then the environmental efficiency of worn and original samples was measured using microscopic analysis. Figure 3.6 presents the results.




*Source: Hassan et al., 2012b*

*Figure 3.6 NO Removal Efficiencies for Original, Worn, and Abraded Samples*

They noted that in assessing for environmental effectiveness after wear and abrasion,

> "it appears that the Load Wheel Tester slightly improved the NO removal efficiency of the different samples with the exception of samples with 5% TiO2, which experienced a slight decrease in efficiency. This result may be due to the wear action simulated using the LWT, which exposed part of the embedded titanium dioxide particles at the surface and therefore improved the NO removal efficiency. In contrast, rotary abrasion appears to result in a decrease in NO removal efficiency for the 5% TiO2 coating and the PT product while the efficiency slightly improved or remained constant for the other specimen types. In general, the samples coated with 5% TiO2 and the PT product were the most efficient in removing nitrogen oxide from the air stream. The highest NO removal efficiencies in the original and RA states were measured for the coating with 5% TiO2. On the other hand, the highest NO removal efficiency in the LWT state was measured for the samples treated with the PT product" (Hassan et al., 2012b pp 604).

Guerrini et al. in 2012 at the 10th International Conference on Concrete Pavements highlighted investigative projects conducted on photocatalytic roadway/tunnel coverings at three sites in the E.U.: in Bergamo, Italy, on a city road built of paving blocks; on a concrete city road in Paris, France; and a city road tunnel in Rome, Italy. All three in-situ experimental projects had been shown to have positive results (Guerrini et al., 2012).

Boonen and Beldens in 2012 reported on further E.U.-funded in-situ projects in Belgium, showing the differences from laboratory tests through to a pilot project in Antwerp. The on-site studies took measurements of air at 5 cm above the photocatalytic surface, and found that $NO_x$ concentration did decrease (Boonen and Beldens, 2012).

In 2012 Churchill and Panesar looked at the life cycle cost analysis of highway noise barriers designed with photocatalytic cement (Churchill and Panesar, 2012). They found that:

"A key outcome from this study revealed that at a 40-year service life, assuming a 6 mg/h/$m^2$ $NO_x$ degradation rate, a barrier designed with 100% General Use (GU) cement and a 25 mm photocatalytic concrete cover has an annual cost that is 7%, 30%, and 36% greater than the 100% GU, 35% and 50% Ground Granulated Blast Furnace Slag (GGBFS) barriers without a photocatalytic cover, respectively. Results of this analysis also indicated that the application of a 25 mm photocatalytic concrete cover to concrete containing 35 and 50% GGBFS is more economically feasible than 100% GU concrete, irrespective of the service life and pollution degradation rate" (Churchill and Panesar, 2012, pp 983).

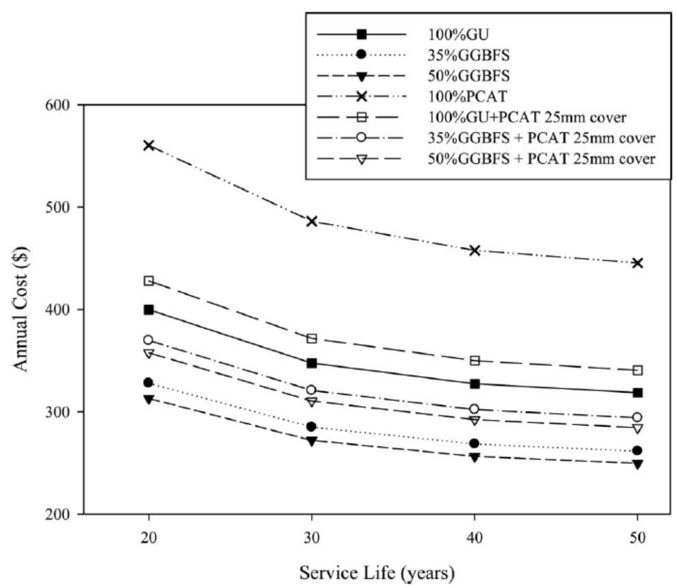
They conducted a series of test and determined the annual cost of base case accounting for $NO_x$ and $PM_{10}$ degradation, as Table 3.5 displays.

**Table 3.5 Annual Cost of Base Case Accounting for $NO_x$ and PM10 Degradation**

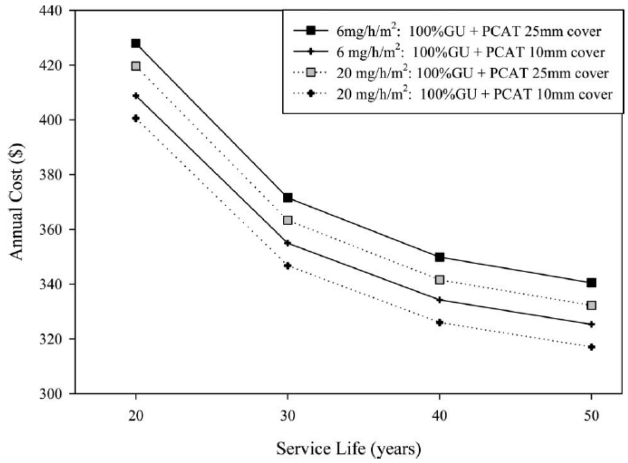
| $NO_x$ degradation ($mg/h/m^2$) | Service life (years) | Barrier design | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | D1 | D2 | D3 | D4 | D5 | D6 | D7 | D8 | D9 | D10 |
| 6 | 20 | 400 | 328 | 313 | 555 | 425 | 367 | 355 | 400 | 406 | 413 |
| 6 | 30 | 348 | 285 | 272 | 481 | 369 | 318 | 308 | 347 | 352 | 358 |
| 6 | 40 | 327 | 268 | 256 | 452 | 347 | 299 | 290 | 326 | 332 | 337 |
| 6 | 50 | 319 | 261 | 250 | 440 | 338 | 291 | 282 | 318 | 323 | 328 |
| 20 | 20 | 400 | 328 | 313 | 538 | 417 | 359 | 347 | 392 | 398 | 404 |
| 20 | 30 | 348 | 285 | 272 | 464 | 361 | 310 | 299 | 339 | 344 | 350 |
| 20 | 40 | 327 | 268 | 256 | 436 | 339 | 291 | 281 | 318 | 323 | 329 |
| 20 | 50 | 319 | 261 | 250 | 423 | 330 | 283 | 273 | 309 | 314 | 319 |

*Source: Churchill and Panesar, 2012 pp 990*

They then reviewed the effect of GGBFS as a cement replacement and then the influence of $NO_x$ degradation rate and P these results.




*Notes: $NO_x$ degradation rate: 5mg/h/$m^2$*
*Source: Churchill and Panesar, 2012 pp 991*
*Figure 3.7 Effect of GGBFS as Cement Replacement and PCAT Concrete Cover on Annual Cost*




*Source: Churchill and Panesar, 2012 pp 991*

*Figure 3.8 Influence of $NO_x$ Degradation Rate and PCAT Cover Thickness on Annual Cost*

Their report states the following:

> "The composite barrier designed with 100% GU cement and a 25 mm photocatalytic concrete cover has an annual cost that is 7, 30 and 36% greater than the 100% GU, 35% GGBFS and 50% GGBFS barriers without a photocatalytic cover, respectively at a service life of 40 years, and a 6 mg/h/$m^2$ $NO_x$ degradation rate. For a degradation rate of 20mg/h/$m^2$, the annual cost of the barrier designed with 100% GU and a 25 mm PCAT concrete cover is greater than the100% GU, 35% GGBFS, and 50% GGBFS barriers by 4, 27 and 33%, respectively. At all service lives, the noise barrier designs that add 25 mm photocatalytic concrete cover to a concrete base containing 35% and 50% GGBFS as cement replacement are more economically feasible than 100% GU concrete for both the 6 and 20 mg/h/$m^2$ $NO_x$ degradation rates. For a service life of 40 years barriers with 35 and 50% GGBFS have annual costs that are respectively, 7.7% and 10.7% less than the design with100% GU with a 6 mg/h/$m^2$$NO_x$ degradation rate and 10.3% and 13.3% less when the $NO_x$ degradation rate is 20 mg/h/$m^2$.The noise barrier designs with the thinnest photocatalytic concrete covers, namely 5 mm(mix D8) and 10 mm (mix D9), are more economically feasible compared to barriers de-signed with 100% GU without photocatalytic cover (mix D1), for service lives which are 30 years or greater, modelled with a $NO_x$ degradation rate of 20 mg/h/$m^2$. Combining thin covers with a base that contains GGBFS is the most economically feasible alternative. Increasing the pollution degradation rate from 6to 20 mg/h/$m^2$ reduces the annual cost by approximately 2.4% irrespective of the photo-catalytic cover thickness. However, at a degradation rate of 20 mg/h/$m^2$ the barrier with a 10 mm photocatalytic cover thickness is more economically feasible than a 100% GU barrier without a photocatalytic cover when the cost of $NO_x$ exceeds approximately $9000/tonne" (Churchill and Panesar 2012, Pp 995).

They conclude by noting:

> "The overall findings from this study indicate that photocatalytic cement has potential to be a socially, environmentally and economically feasible alternative for concrete noise barriers. It is however imperative to achieve high $NO_x$ degradation rates for photocatalytic concrete barriers to become economically feasible. Selection of the orientation, geometry and exposed surface area of infrastructure containing photocatalytic cement should be carefully considered since the light intensity, relative humidity and wind characteristics influence the effectiveness of the photocatalytic processes…The influence of the degradation of particulate matter increases the annual cost savings through pollution reduction by 75%. Even though the pollution avoidance cost for particulate matter is quite high compared to other pollutants, the amount of particulate matter that can be degraded is still small due to the low, 19–300mg/$m^3$, pollutant concentrations on primary road networks in Canada" (Churchill and Panesar 2012, Pp 995).

Hassan et al. in 2013 noted that field test of photocatalytic pavement technologies in the U.S. was still de minimus:

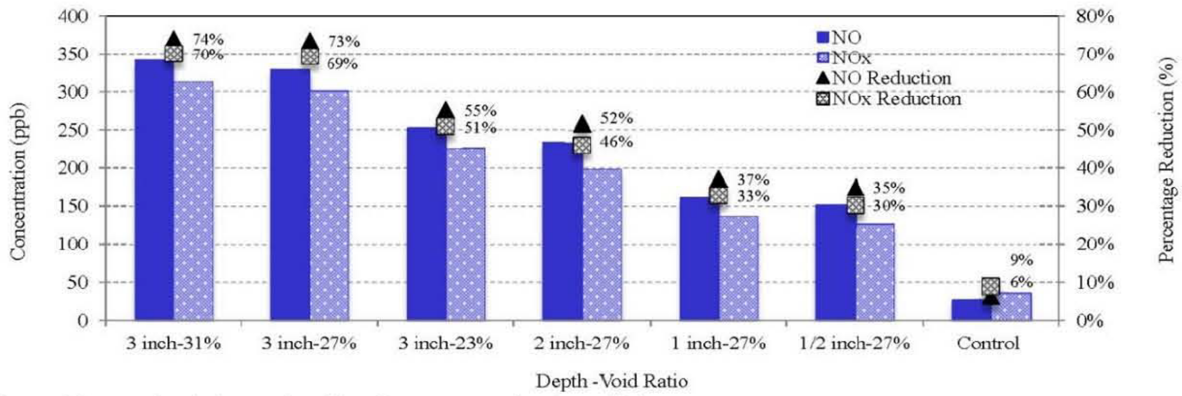
> "to date, field evaluation of photocatalytic pavement technology has been limited. Hassan and co-workers laid the country's first air-purifying photocatalytic asphalt and concrete pavements on December 20, 2010…on the Louisiana State University (LSU) campus: A customized distributor truck was used in the application of a $TiO_2$ water-based solution. Two parameters were necessary to remain constant during the application: speed and pressure. To maintain an accurate and steady speed of 50 foot per minute min, a magnet was placed on the drive shaft that counted each revolution. The distance covered per revolution was calibrated by counting the number of rotations, as the truck drove 100 feet."

In this study Hassan et al. were looking at the sustainability of photocatalytic asphalt pavement for $NO_x$ and $SO_2$ emission abatements. The field experiment looked at the direct measurement of $NO_x$ reduction and the indirect measurement of $NO_x$ reduction through nitrate analysis. Again, the researchers noted that the proper method to apply $TiO_2$ was unclear. Their results showed that $TiO_2$ was effective in removing $NO_x$ in the laboratory at an efficiency range between 31 and 55%. $TiO_2$ was also effective in removing $SO_2$ pollutants, with a reduction efficiency of 19.8%. For the field test they noted that *"Results of the direct method and indirect methods of measuring photocatalytic degradation of $NO_x$ show that there is evidence of a photocatalytic reaction occurring in the field"* (Hassan et al., 2013). This research as also reported out at the TRB 2013 annual meeting with David Osborn as lead author (Osborn, 2013).

In an indoor test conducted in Italy on Smart Tiles by Sannino et al. in 2013 (Sannino et al., 2013), the use of $TiO_2$ sprayed onto floor tiles in an indoor office environment was shown to completely remove $NO_x$ from the air stream without deactivation of the $TiO_2$ film.

Asadi et al. (part of Marwa Hassan's team at Louisiana State) in 2013 (Asadi et al., 2013) evaluated $NO_x$ and NO removal efficiency with different void ratio and $TiO_2$ depths in pervious concrete in a series of laboratory experiments. Their results found that $TiO_2$ was effective in removing $NO_x$

pollutants with an efficiency ranging from 30% to 70%. The maximum amount of $NO_x$ removal occurred at 3 inches depth of $TiO_2$ with a void ratio of 31% (Figure 3.9).




*Source: Asadi et al., 2013*

*Figure 3.9 Effects of the Depth of TiO2 and Void Ratio on $NO_x$ Reduction Efficiency*

Mohammed in 2014 reviewed the influence of nano materials on flexural behavior and compressive strength of concrete. He found that

> "Mechanical properties have been investigated such as compressive and flexure strength through testing concrete prisms 40, 40 and160 mm at 7, 28 and 90 days in order to explore the influence of these nanoparticles on the mechanical properties of concrete. Results of this study showed that nanoparticles can be very effective in improving mechanical properties of concrete, nano-silica (NS) is more effective than nano-clay (NC) in mechanical properties and wet mix gives higher efficiency than dry mix. Exceeding a certain percent-age of nanoparticles in concrete negatively affects the mechanical properties. Also, binary usage of nanoparticles; (NS + NC) had a remarkable improvement appearing in concrete compressive strength than using the same percentage of single type of nanoparticles. This improvement can be attributed to the reaction of nanomaterials with calcium hydroxide $Ca(OH)_2$ crystals, which are arrayed in the interfacial zone (ITZ) between hardened cement paste and aggregates, and produce C-S-H gel and the filling action of nanoparticles which cause more densified microstructure. A percent of 3% nanoparticles consisting of 25% NS and 75% NC gave the highest mechanical properties representing in both compressive and flexure strengths among other percentages (Mohamed, 2014, pp 212).

In 2014 Dylla et al. (Dylla et al., 2014) (part of Marwa Hassan's team) moved to look at the reduction of nitrogen monoxide through degradation using $TiO_2$ nanoparticles. In this study they developed an environmental model to assess the photocatalytic reaction kinetics of NO reduction under varying environmental conditions. Again they noted that the current understanding of photocatalytic pavements in real world settings was lacking. In reviewing the chemical properties they noted that the reaction scheme that irradiation and the absorbed reactants (water, $O_2$, and NO) all play a role in the PCO. They set up a photoreacter in their lab and used a typical meteorological year to determine their environmental parameters. They found that the "NO reduction per initial concentration at 51% relative humidity and 2.1 $mW/cm^2$ light intensity. As the concentration increases, the percentage of NO degradation decreases, which was the trend for all the tested run scenarios" (Dylla et al., 2014). They concluded that further research was needed to develop a NO reaction rate model for photocatalytic pavements to understand real-world environments and reactions because:

> "The results of the parametric study identified that the relative humidity and light intensity both had a significant impact on the L-H constants and there was an interaction effect between the relative humidity and light intensity. The impact of the relative humidity played a significant role on the L-H equilibrium constant, Kd. Contrary to theory, as the humidity increased, the Kd increased, suggesting that additional phenomena to the typical competition of adsorption sites between water and the pollutant play a role in the Kd adsorption, including NO diffusion and dissolution in water. Irradiance significantly affects the reaction rate, k. With higher irradiance, more energy creates more active sites" (Dylla et al., 2014).

In 2014 members of this same team (Osborn et al., 2014) produced papers for TRB and ASCE's *Journal of Materials in Civil Engineering* on the durability quantification of $TiO_2$ surface coating on asphalt and concrete pavements. They found that their results suggested that the durability of a $TiO_2$ treated photocatalytic pavement resulted in a service life for a concrete pavement between 6 and 11 months and for an asphalt pavement between 10 and 16 months (Osborn et al., 2014).

In 2015 Nadiri, Hassan, and Asadi began work on developing a model, based on field data they collected, to predict the $NO_x$ reduction from using a $TiO_2$ nanoparticle pavement coating (Nadiri et al., 2015). A *"supervised intelligent committee machine (SICM) method as a combinational black box model was used to predict $NO_x$ concentration at the pavement level before and after $TiO_2$ application on the pavement surface."* They used three AI models—Mamdani fuzzy logic, artificial neural network, and neuro-fuzzy—to predict $NO_x$ concentration in the air as a function of traffic count and climatic conditions (temperature, humidity, solar radiation, and wind speed) before and after $TiO_2$ was applied. Their results indicated that the SICM model could provide a reasonable better prediction of $NO_x$ concentration as an air pollutant (the model had less mean square error than using multivariate regression models) (Nadiri et al., 2015).

Verbruggen in 2015 (Verbruggen, 2015) looked at $TiO_2$ photocatalysis for the degradation of pollutants in the gas phase. In looking at porous and interconnected and supported structures, he noted that:

> "Although quite some benefits are associated with the use of nanoparticles, a big disadvantage is that they have high tendency to agglomerate into larger aggregates. Generally this is at the expense of photocatalytic activity, but in particular cases it can also lead to an improved efficiency. Bahnemann's group have proposed the 'antenna mechanism', which involves the transfer of photon energy from one nanoparticle to another when they are arranged as an interconnected network along a fixed crystallographic

orientation. This could be an important effect in many $TiO_2$ powders consisting of large secondary agglomerates of closely interconnected crystalline nanoparticles. In many other cases, however, $TiO_2$ nanoparticles are incorporated into (porous) substrates or alternatively, (ordered) interconnected 3D structures of pure $TiO_2$ are synthesized" (Verbbruggen, 2015 pp 70).

Verbruggen concludes his review by noting that

> "From a socio-economic perspective, photocatalytic air purification still offers great opportunities. Already 15 years ago, Fisk estimated that the productivity gains that may be obtained by improving indoor air quality in the United States amount to 6–14 billion USD by reducing respiratory diseases, 1–4 billion USD by reducing allergies and asthma, 10–30 billion USD from decreased Sick Building Syndrome (SBS) symptoms and 20–160 billion USD dollars by improving general worker performance. In that regard it is surprising that a BCC Research market survey from 2010 reported that only 0.5% of the total photocatalyst product sector is directly related to environmental applications. The largest share (87.4%) is accounted for by the construction sector (photocatalysts in building materials).It has to be noted that the latter can also indirectly exert a beneficial influence on the environment, mainly through passive systems (e.g. coated surfaces exposed to the surrounding environment). Given these appealing prospects and the ample room for growth in the photocatalyst sector for environmental applications, it is wise not only to focus on improving the performance of photocatalysts through all kinds of high-end modification methods, but also keep taking into account the resulting costs, especially with the eye on commercialization."

Macphee and Folli in 2016 looked at photocatalytic concretes and the interface between photocatalysis and cement chemistry. Their research addressed *"(i) the photocatalytic mechanisms applicable to atmospheric depollution, (ii) the influence of doping, and (iii) the application of* $TiO_2$*- based photocatalysts to concrete. Modifications to* $TiO_2$ *will be discussed which can improve its activation in visible light and, in the treatment of* $NO_x$*, improve catalytic selectivity towards nitrate rather than the more toxic* $NO_2$*."* Their findings looked at a number of key physico-chemical factors, among others, and noted that:

> "Pollutant degradation must be viable based on oxidation potentials relative to semiconductor band edge positions—these are pH dependent.
>
> Geographical limitations of photocatalytic concrete will not be over-come by conventional $TiO_2$—more fundamental research is needed to optimize the photonic efficiencies of visible light photocatalysts.
>
> Catalyst surface area must be maximized for the target application; care must be taken to ensure particle dispersion is optimized. Agglomeration can block access to internal surface, i.e. if pollutant molecule size is greater than pore entry diameter.
>
> Conventional $TiO_2$ is often very unselective and exhibits large negative $DeNO_x$ index, a sign of ineffective catalytic process (too much $NO_2$ is released). Increasingly photocatalyst

selectivity, not only activity, is required to reduce emission of harmful by-products" (Macphee and Folli, 2016 Pp 54).

Nayak et al. in 2016 (Nayak et al., 2016) reviewed the effects of surface carbon on the visible-light photocatalytic activity of nitrogen doped $TiO_2$-C nanocomposite powder. In his method he used nitrogen doped $TiO_2$-C composite nanoparticles and the powder and structures were analyzed by X-ray photoelectron spectroscopy, and X-ray diffraction and transmission electron microscopy and optical properties was studied by UV-visible light absorption. The visible photocatalytic activity of black $TiO_2$ powder was investigated by studying the photobleaching of methylene blue under solar irradiation. The effect of surface concentration of the carbon and nitrogen on the visible photocatalytic efficiency of the black-$TiO_2$was assessed. White $TiO_2$ powder without surface carbon was also synthesized and compared with that of the black $TiO_2$ powder. Nayak et al. found that:

> Black $TiO_2$ was purely anatase whereas white $TiO_2$ had mixed phase character with 68% anatase and 32% rutile. Compared to white $TiO_2$, black $TiO_2$ could absorb more visible light. Unlike white $TiO_2$, Black $TiO_2$ is an efficient solar photocatalyst responsible for the photodegradation of 52 µM aqueous solution of MB with a first order rate constant, k = 0.02 min-1. The photocatalytic activity of black-$TiO_2$ strongly depended on the surface carbon concentration. The photo-catalytic activity of black-$TiO_2$ increases with increased carbon content. When the surface concentration exceeded 28%, the catalytic activity decreased presumably due to slower rate of charge transfer onto the $TiO_2$ nanoparticle surface. No such systematic change in the photocatalytic activity of black-$TiO_2$ was observed with change in its N content.

In 2017 Singh et al. undertook a review of the nanoscience of cement and concrete. They concluded "currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients. Concrete science is a multidisciplinary area of research where nanotechnology potentially offers the opportunity to enhance the understanding of concrete behavior, to engineer its properties and to lower production and ecological cost of construction materials" (Singh et al., 2017 pp 5486).

Research is also currently looking at sensor capacity and nanotechnology. For example, Tang et al. in 2017 looked at a formaldehyde sensor based on a molecularly imprinted polymer on a $TiO_2$ nanotube array (Tang et al., 2017).

Faraldos and Bahamonde in 2017 in *Catalyis Today* began to look at the use of titania graphene photocatalysts. They began by noting that:

> "Recently, graphene is receiving great attention in the area of photocatalysis…and emerging in the next generation of photocatalysts, as a tool for enhancing photocatalytic performance and solar photo efficiency. Titanium dioxide hybridization with graphene has an effect on band gap energy decrease, shifting its absorption threshold to the visible light region and allowing it to harness solar energy. So, the conjugation of graphene with

> semiconductor solid particles such as $TiO_2$, results in photocatalysts with improved charge separation, reduced recombination of the photo generated electron-hole pairs, increased specific surface area, and introduces an adequate quantity and quality of adsorption sites, given that enhances their electronic, optoelectronic, electrocatalytic and photocatalytic properties."

In their review of the literature they noted that there were few papers on $TiO_2$ graphene composites for air pollution, and few looking at their use in photocatalytic waste water applications. The use of nanotechnology for reduction of waste water pollutants may be a further area that TxDOT may want to review. They conclude by noting that *"It is necessary to widen the scope where photocatalytic applications of graphene oxide-titanium dioxide composites could be useful: different pollutants, real water effluents, self-cleaning materials, biocide coatings, etc. are fields that still need to be explored"* (Faraldos and Bahamonde, 2017 pp 27).

Norhasri et al. in 2017 conducted another review of applications of using nano material in concrete (Norhasri et al., 2017). They reviewed nano silica, nano alumina, carbon nanotube, polycarboxylates, titanium oxide nano kaolin, and nano clay and found that the addition of ultrafine nano materials aided in formation of micro pores and acted as a filler agent to produce a denser concrete.

Reches in 2018 also reviewed nanoparticles as concrete additives (Reches, 2018). He found that "Nanoparticles are highly efficient additives for modification of cement products, even at small concentrations (≤1%). The main modifications are (typical ranges shown, though great variability has been observed): reduction of set time (by 1–2 h) and diffusivity (by 4–75%), and increase of strength (by 5–25%), and thermal durability (0–30% increase in residual strength)" (Reches, 2018). These modifications were attributed to the unique reactivity of nanoparticles associated with their small size and large surface area. The paper reviewed $SiO_2$, $Al_2O_3$ [aluminum oxide], $Fe_2O_3$ [ferric oxide], $TiO_2$, $CaCO_3$ [calcium carbonate], and clay nanoparticles, and assessed effective modification mechanisms and potential commercial application challenges, including cost and dispersion. He concluded that further that

> "Optimization of technologies and protocols for dispersing NPs, and for characterizing their dispersion state in situ in the cement products. The use of nano-powders does not apparently accommodate good dispersion; and while sonication with or without dispersing agents improves dispersion, NPs remain in large agglomerates. It seems crucial that cement researchers will need to become involved in the synthesis of NPs designed with their needs in mind, including particularly the application of a ligand to maintain mono-particle-dispersion, while taking care that any ligand does not hamper the functions of the NPs, OPC, or admixtures" (Reches, 2018, pp 493).

A field study survey of the $NO_x$ removal efficiency of catalytic in a Korean expressway was reviewed in 2018 by Kim et al. (Kim et al., 2018). In this test experiment on a real-world road, Kim et al. used surface penetration agents to add $TiO_2$ to the surface of the concrete structure. The study evaluated the in-situ $NO_x$ removal efficiency of the $TiO_2$ penetration method on the retaining wall of the Gyeongbu expressway in Korea. The results indicated that the quantity of sunlight influenced the $NO_x$ removal efficiency rate. The research team determined that the $TiO_2$ penetration method can be an alternative to using existing $TiO_2$ concrete. The results found that after the penetration method of applying $TiO_2$ took place, the $NO_x$ concentration removal rate was approximately 0.07 ppm, or about 13% efficiency in removing the pollutant. The $TiO_2$ penetration method, applied as a mixture of $TiO_2$ and surface penetration agents at 500 $g/m^2$, was determined to be a feasible alternative method for removing the $NO_x$ gases in areas with a high volume of traffic (Kim et al., 2018).

Leng et al. in 2018 reviewed the air-purifying performance of asphalt mixtures coated with $TiO_2$. They custom-designed an environmental test setup to determine the $NO_X$ degradation efficiency of their specimens with $TiO_2$ coating, and the durabilities of the coating materials were characterized by measuring their $NO_x$ degradation efficiency subjected to different numbers of lab-simulated tire abrasion (Leng et al., 2018). They used three coating methods (Table 3.6) and preparation processes and had one control group (Table 3.7). Figures 3.10 and 3.11 present the results.

**Table 3.6 Preparation of Three Coating Solutions**

| Coating method | Materials | Preparation process |
|---|---|---|
| WT | Water and $TiO_2$ | Mixing $TiO_2$ particles directly with water by magnetic stirring for 40 min |
| PT | Tetrahydrofuran (THF), polystyrene (PS), asphalt binder, and $TiO_2$ | Mixing asphalt binder, THF, PS, and $TiO_2$ together by ultrasonic dispersion and magnetic stirring for 40 min and 2 h, respectively |
| GT | Glass bead, coupling agent, ethyl alcohol and $TiO_2$ | Mixing $TiO_2$ and coupling agent KH570 and enough amount of alcohol at 60 °C, followed by ultrasonic dispersion for 1 h |

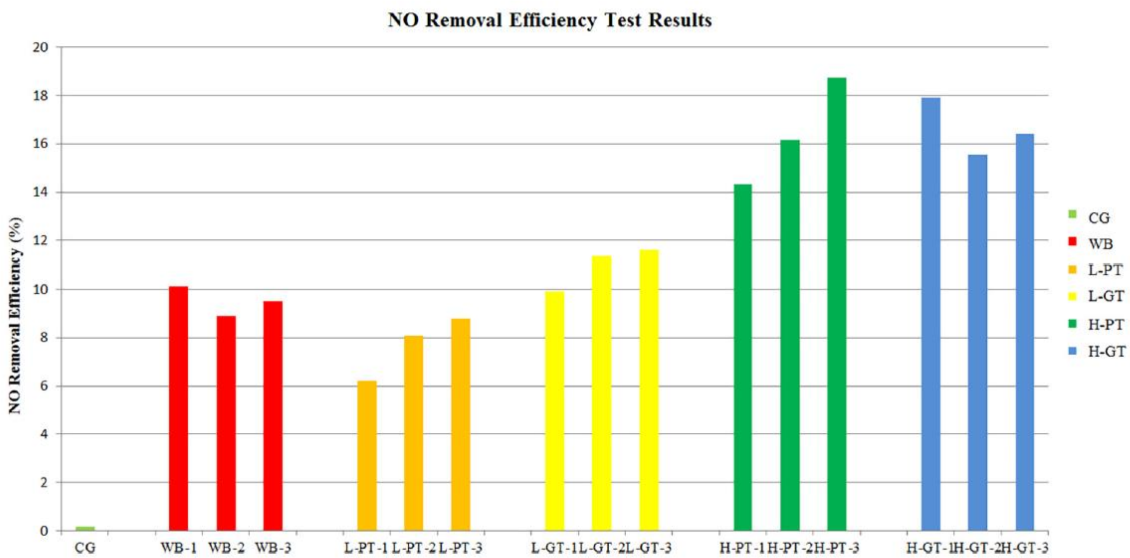
*Source Leng et al., 2018, pp 4*

**Table 3.7 Test Groups**

Marshall specimens with different coating solutions.

| Group ID | $TiO_2$ content on each sample | Number of samples |
|---|---|---|
| CG (control group) | 0 g | 3 |
| WTM (mixture with water-based $TiO_2$ coating) | 0.4 g | 3 |
| L-PTM (mixture with low rate porous $TiO_2$ coating) | 0.1 g | 3 |
| H-PTM (mixture with high rate porous $TiO_2$ coating) | 0.4 g | 3 |
| L-GTM (mixture with low-rate glass-bead-based $TiO_2$ coating) | 0.1 g | 3 |
| H-GTM (mixture with high-rate glass-bead-based $TiO_2$ coating) | 0.4 g | 3 |

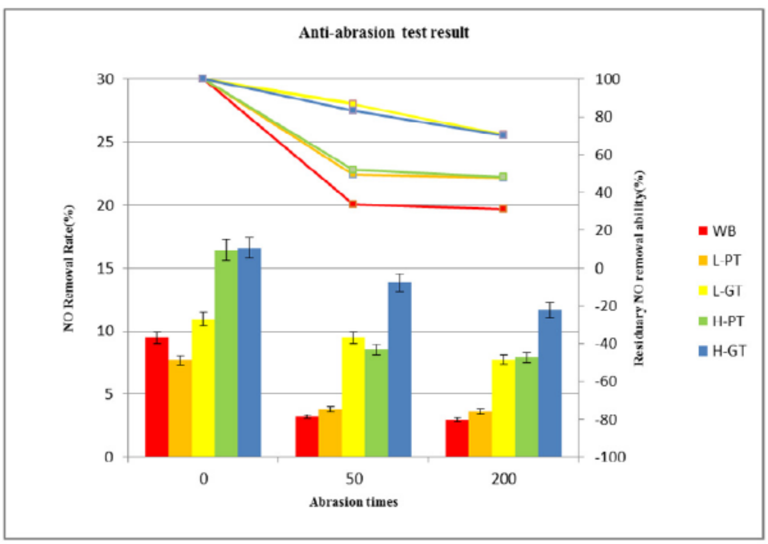
*Source Leng et al., 2018, pp 4*




*Source Leng et al., 2018*

*Figure 3.10 NO Removal Efficiency Results*

They found that "both the two novel coating methods, PT and GT, pro-vide better $NO_x$ removal efficiency than the conventional WB coating method. The GT method provides the coating material the best abrasion resistance, followed by the PT method and WB method. Considering the removal efficiency and durability, GT is the most promising coating method to incorporatenano-$TiO_2$ particles onto asphalt pavement" (Leng et al., 2018).



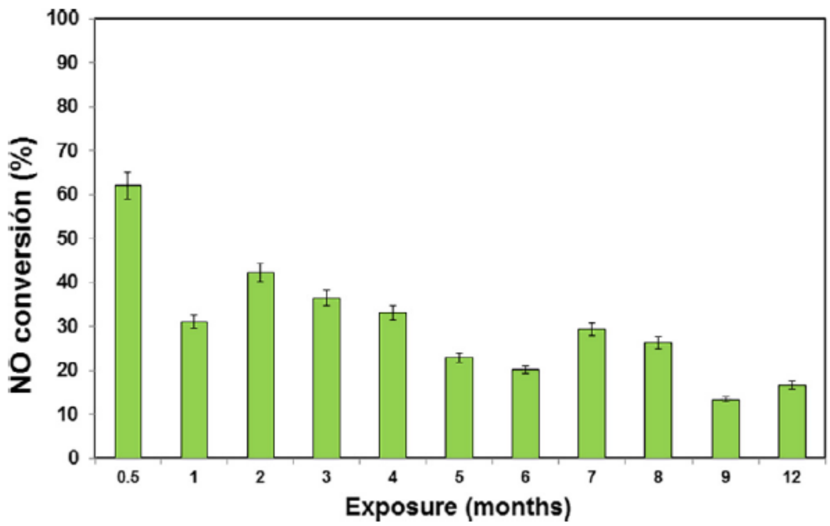

*Source: Leng et al., 2018*

*Figure 3.11 Durability Results*

Luevano-Hipolito and Martinez-de la Cruz in 2018 reviewed the use of $TiO_2$ in stucco for $NO_x$ removal by real weatherism (Luevano-Hipolito and Martinez-de la Cruz, 2018). They created an artificial weathering chamber and aged the stucco over 14 days. The test blocks were then placed into a chamber and removed every 100 hours with total exposure time set at 1000 hours. They noted that:

> "the formation of $CaCO_3$by carbonation reaction gradually blocks the porosity of the coating, which impacts negatively the specific surface area property. The biggest decrease in the surface area value took place during the first 100 hours of treatment. However, the decrease in the value of surface area seems not affect significantly the photocatalytic activity of $CleaNO_x$. In this regard, the $CaCO_3$ forming by the carbonation reaction can help to maintain the activity by promoting the absorption of $NO_x$ gases in the coating surface. In this context, it has been reported the use of $CaCO_3$ as absorber of gaseous pollutants such as $NO_x$ and $SO_x$ in flue gas." (Luevano-Hipolito and Martinez-de la Cruz 2018, pp 306

After these initial findings they then aged their samples in the open air for a year. Figure 3.12 shows the $NO_x$ conversion over the months.




*Notes: P-25 Exposed at Weathering Conditions During Year 1 (Q = 1L min $^{-1}$, I = 10.1 W m$^{-2}$, RH = 70%*
*Source: Luevano-Hipolito and Martinez-de la Cruz 2018, pp 308*
*Figure 3.12 NO Conversion Degree Using Photocatalytic Coating with TiO2*

They concluded that:

> "The development of the construction material $CleaNO_x$ with photo-oxidative active surface for removal of NO by the action of solar radiation is proposed. In addition, the photocatalytic coating has the ability to capture $CO_2$ from air by means of a carbonation process. The active material $TiO_2$SG7 synthesized was a result of an optimization of the synthesis method in order to have a photocatalyst with an efficient NO conversion degree. The results indicated that the introduction of the active oxide in the inorganic matrix has a dilution effect on the photocatalytic activity, however its photocatalytic activity was retained after the incorporation in the matrix. The exposure of the coating to weathering conditions promoted the carbonation of the surface, which product tends to block the active

sites and decrease the photocatalytic activity by a poisoned effect. Also, the coating can storage dust or material particulate from the environment, which had a detrimental effect in the photocatalytic activity. This poisoning can be removed by a washing process, and after that, the surface coating maintained almost its original photocatalytic activity. In addition, when the coating was exposed under weathering conditions for 1 year, the results show that it requires a humid environment with relative low temperatures to promote an efficient removal of NO and $CO_2$ gases" (Luevano-Hipolito and Martinez-de la Cruz 2018, pp 308).

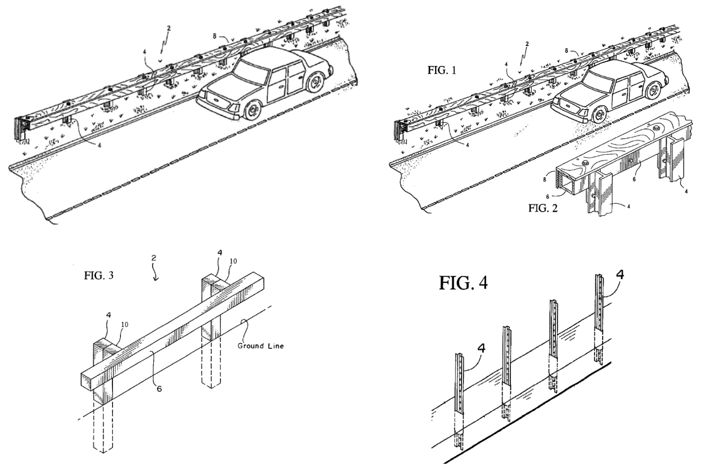
Papoulis, in 2019, looked at halloysites-based nanocomposites and photocatalysis as a promising area for review and to improve on a known adverse catalytic impact seen in $TiO_2$: agglomeration into larger particles over time (Papouis, 2019). Halloysite nanotubes are found in natural clay, and can facilitate modification and growth of other functional materials for PCO. While halloysite is not a photocatalyst in itself, in combination with other photocatalysts or if it is used as a substrate, it improves the PCO of the end material. This is due to the high BET surface area, whereby high absorptivity heightens interaction with a nano-product and promotes the photocatalytic properties. In the Papoulis review of photocatalytic decomposition of inorganic air pollutants, volatile organic compounds (VOCs), Azo dyes, and photocatalytic decomposition of antibiotics/drug components/pesticides the study assessed the use of halloysite $TiO_2$ nanocomposites in various papers. All the papers and tests were found to have promise. However, Papoulis noted that only $NO_x$ decomposition had been measured with some modification of halloysite with another technique and the paper suggested further research was needed to test.

### 3.2.1. U.S. Patent Applications

The literature review search discovered a few patent applications for nanotechnology and highway use. The most relevant is U.S Patent application 2005/0159309 A 1, July 2005 by Hubbell et al., which envisioned:

"A highway Safety equipment System using Solid catalyst crystal, Such as titanium dioxide, targeted for the breakdown of fluid borne undesirable material, Such as "Smog utilizing Standard, commonly encountered, U.S. Federal Highway Administration (FHWA), National Cooperation Highway Research Program (NCHRP), and/or American Association of State Highway and Transportation Officials (AASHTO) Standard Specification items. Such as highway guiderail, highway signing, highway Signal equipment, housings, toll booth, bridgework, bridge rails and/or Such items Support Structures…the present invention utilizes the teachings of U.S. Pat. No. 6,676.279 (279) and U.S. Pat. No. 6,705,744 (744) to Hubbell, et al. (a co-inventor of the present invention). Patents 279 and 744 teach that prior art systems for illuminating large, distant areas generally are deficient in that they produce light pollution, confusing night time driving conditions, light trespass, glare, energy waste, high maintenance cost and contribution to urban sky glow. The present invention is directed to a need to provide an area lighting and/or other wavelength radiation device that avoids the shortcomings of the prior art lighting Systems."

A search of the U.S. Patent Office database does not show this patent as being approved. Figure 3.13 provides the drawings included in the application.




*Source: U.S. Patent and Trade Mark Office*
*Figure 3.13 United States Patent Application*

### 3.2.2. The Hype Around Nanotechnology and Emission Reduction

The literature review also revealed that as in many disruptive type technologies, there is much hype surrounding the ability of nanotechnology to achieve its potential goals. There is also growing concern that the use of nanotechnology will have unintended consequences. The literature review revealed that much of the research conducted to date has been in a laboratory setting, is expensive, and has focused upon a singular product in the transportation setting. Making the jump out of the Valley of Death into the Middle Ground (to use the GAO's terms) has yet to be achieved. In the context of the concrete industry—which provides immense quantities of product at globally set prices in an industry that some might call "old fashioned"—emission-reduction nanotechnology's ability to find a home will require reliable and cost-efficient products that are replicable in any geoclime and for any type of mode. Raki et al. (Raki et al., 2010) noted that:

> "the nature of the construction industry is such that it is easier to implement process innovations, rather than disruptive product innovations. Construction integrates products from a wide range of suppliers and skills from a wide range of contractors, subcontractors and trades into a single finished structure. A change in the way a structure is built can be determined by the construction company itself, but a significantly new product needs to be created by a supplier, understood and approved by architects, engineers and the client and implemented by on-site workers who may need to be specifically trained in its use.
>
> All of these factors must be taken into consideration in developing nanotechnology for use in concrete. First, concrete and related products are bulk commodities. Even high value concrete structures require low materials costs and the ability to handle large quantities of material in a safe and environmentally acceptable manner. Second, innovations need to be thoroughly developed and field tested in order to build the knowledge and confidence in

> the construction community. Finally, concrete structures can be difficult to demolish, often requiring explosive or other high-energy approaches as an initial step to break up the major components of the structure. Nanotechnology used in concrete must therefore be compatible to these traditional practices.
>
> Given these constraints, the initial nanotechnology applications in construction are those that provide a clear benefit in terms of added functionality with relatively small amounts of nanomaterials that can be delivered in using standard construction practices and will not affect other aspects of the performance of the material. Novel products that improve the delivery of existing materials, such as the control released admixture work described here, are likely to be next to market. Other innovations, such as nano calcium carbonate accelerators, will become more common as the price of the nanomaterial falls to the point where it can be used in bulk. Carbon nanotube/cement composites, in contrast, will likely take the longest time to implement as they will require further fundamental research, reductions in CNT [carbon nanotube] prices, the development of specialized delivery techniques and equipment, greater understanding of the environmental impact of CNTs and specialized demolition methods before wide spread adoption can occur."

Raki et al. also noted that "A key factor to economic viability is the need for the cost of the nanoparticles to be lower than the cost of the cement that is replaced. This condition in turn implies that much lower nanoparticle contents should be used in the blend than the percentage of cement that was replaced. Providing this condition is met, significant economic benefits are possible through reduction of the amount of cement used in a structure" (Raki et al., 2010).

Concerns are also being raised on the toxicology of nano technology—what could be called the *unintended consequences*. The CRS and GAO have noted that further studies are needed in this area. Schmid et al., in a 2009 article in *Biomarkers*, looked at dosimetry and toxicology of ultrafine particles (<100nm) on the brains, lungs, and major pathways. They found that "BET surface area is emerging as the single most relevant dose parameter for particle toxicity both in the ultrafine (<100 nm) and fine (100–2500 nm) size range" (Schmid et al., 2009).

The GAO noted in its May 2010 report (GAO, 10-549, 2010) that:

> "The extent to which nanomaterials present a risk to human health and the environment depends on a combination of the toxicity of specific nanomaterials and the route and level of exposure to these materials. Although the body of research related to nanomaterials is growing, the current understanding of the risks posed by these materials is limited. This is because the manner in which some studies have been conducted does not allow for valid comparisons with newer studies or because there has been a greater focus on certain nanomaterials and not others. Moreover, the ability to conduct necessary research on the toxicity and risks of nanomaterials may be further hampered by the lack of tools to conduct such studies and the lack of models to predict the characteristics of nanomaterials.
>
> EPA has undertaken a multipronged approach to understanding and regulating the risks of nanomaterials, including conducting research and implementing a voluntary data collection

program. Furthermore, under its existing statutory framework, EPA has regulated some nanomaterials but not others. Although EPA is planning to issue additional regulations later this year, these changes have not yet gone into effect and products may be entering the market without EPA review of all available information on their potential risk. Moreover, EPA faces challenges in effectively regulating nanomaterials that may be released in air, water, and waste because it lacks the technology to monitor and characterize these materials or the statutes include volume based regulatory thresholds that may be too high for effectively regulating the production and disposal of nanomaterials" (GAO, 10-549, 2010 pp 2).

The GAO in its 2014 report *Nanomanufacturing Emergence and Implications for U.S. Competitiveness, the Environment, and Human Health* noted that:

"Forum participants offered a wide range of perspectives on the environmental, health, and safety (EHS) implications of nanotechnology, nanomanufacturing, and nanomaterials. Forum participants presented information on what is currently known about these implications and expressed frustration about the lack of progress in understanding the risks from potential exposure to nanomaterials. Participants specifically noted a current dilemma related to identifying or determining EHS risks. Because so few nanomaterials have been studied and no long-term or chronic data are available, it is very difficult to predict and manage risks for new nanomaterials. Forum participants also identified significant research needs to discern EHS implications, and they discussed the need to fully communicate the benefits and risks of nanotechnology to the public, helping to distinguish between perceived and real risks" (GAO 14-181SP, 2014 Pp 55).

There is some hype around photocatalytic surface's ability to reduce emissions, and concerns about potential side effects. The UK's Department for Environment, Food and Rural Affairs in 2016 noted that:

"Taken as a whole, there is little current evidence to suggest the widespread use of photocatalytic surfaces will reduce ambient concentrations of $NO_2$. Furthermore, there is a risk that these materials will result in the production of other undesirable species such as nitrous acid and formaldehyde, which can have wider impacts on atmospheric chemistry as well as adverse health impacts. Photocatalytic surfaces can reduce concentrations close to the treated surface but this will not result in significant reductions in $NO_2$ concentrations in the surrounding air. It is not physically possible for large enough volumes of air to interact with the surface under normal atmospheric conditions and therefore this method will not remove sufficient molecules of $NO_2$ to have a significant impact on ambient concentrations" (DEFRA, 2016).

Crispino et al. in 2010 evaluated the long term environmental and functional performances of innovative photocatalytic road pavements. They found in their experiments that:

Data collected from the experiments carried out showed that photocatalytic road materials induced a significant reduction in air pollutants concentration ($NO_x$ reduction up to 40%

were found). Moreover, $TiO_2$ durability was investigated, evaluating the resistance of the photocatalytic emulsion to wearing through the Wheel Tracking Test. The purpose of these tests was to simulate field conditions and long term performances of photocatalytic road pavements, to measure the ability of sprayed bituminous pavements to reduce $NO_x$ during the whole life of the wearing course. *Results showed that increasing load cycles, photocatalytic activity of sprayed material is reduced up to half of the initial value.* Such result also demonstrates the wearing effect from Wheel Tracking Test on sprayed photocatalytic emulsion but the correlation between wearing effects from such device and real traffic is still to be found. Further research is therefore strongly recommended to investigate long term performances of photocatalytic road pavements also in term of economical vantages for the environment."

Hassan, in a 2009 study on the evaluation of the environmental impacts of TiO2 photocatalyst coatings for pavements using life-cycle assessment, also found that

"Life Cycle inventory (LCI) for titanium dioxide coating considers energy and emissions associated with the manufacturing of titanium dioxide, production of aggregate, plant operations, cement and surface mix production, and titanium dioxide coating placement (including transportation to the site and site worker transport). However, the developed LCI *does not consider* energy, materials, and emissions associated with the production or construction of the supporting concrete pavement. In addition, it does not consider energy associated with the production of fuels known as pre combustion, or energy associated with manufacturing of equipment needed to produce titanium dioxide."

Hassan noted that "emissions associated with background processes including production of fuels and equipment were quantified using Input-Output life cycle assessment" (Hassan, 2009).

There has been concern about the trade-offs for nanotechnology and photodegradation intermediates and end products in terms of their impacts on air and water.

Dylla and Hassan in 2013 studied whether nanoparticles and nitrates released to water from photocatalytic pavements were shown to have adverse effects. Here Dylla and Hassan evaluated and measured the amount of $TiO_2$ nanoparticles and nitrates released to water from photocatalytic concrete pavements. Measurement of the amount of nitrates eluted to water was measured after 4.5 hours of PCO of $NO_x$ where the settings were set to induce a high amount of $NO_x$ reduced and nitrates created. They found:

After 4.5 hours of photocatalytic activity, 8.984 μmols of nitrates were released to water accounting for 49% of the theoretical amount of nitrates created. In addition, the amount of the titanium element was measured using inductive coupled plasma atomic emission spectrometry (ICP-AES). Titanium nanoparticles were not detected in any of the water samples (Dylla and Hasan, 2013).

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# Appendix A

**Table A1: Journal Articles on Nanotechnology**

| | Author(s) | Title | Year | Journal | DOI Number or URL |
|---|---|---|---|---|---|
| 1 | Fabjola Bilo, Alessandra Zanoletti, Laura Borgese, Laura E. Depero, and Elza Bontempi | Chemical Analysis of Air Particulate Matter Trapped by a Porous Material, Synthesized from Silica Fume and Sodium Alginate | 2019 | Journal of Nanomaterials Volume 2019, Article ID 1732196, 9 pages | https://doi.org/10.1155/2019/1732196 |
| 2 | D. Papoulis | Halloysite based nanocomposites and photocatalysis: A Review | 2019 | Applied Clay Science, Vol 168 (February 2019) 164-174 | https://doi.org/10.1016/j.clay.2018.11.009 |
| 3 | L.P. Singha, D. Alia, I. Tyagia, U. Sharmaa, R. Singhb, P. Hou | Durability studies of nano-engineered fly ash concrete | 2019 | Construction and Building Materials Volume 194, 10 January 2019, Pages 205-215 | https://doi.org/10.1016/j.conbuildmat.2018.11.022 |
| 4 | Alireza Haghighat Mamaghani, Fariborz, Haghighat, Chang-Seo Lee | Hydrothermal/solvothermal synthesis and treatment of $TiO_2$ for photocatalytic degradation of air pollutants: Preparation, characterization, properties, and performance | 2019 | Chemosphere Volume 219, March 2019, Pages 804-825 | https://doi.org/10.1016/j.chemosphere.2018.12.029 |
| 5 | Lin Qiu, Yuxin Ouyang, Yanhui Fenga, Xinxin Zhang | Review on micro/nano phase change materials for solar thermal applications | 2019 | Renewable Energy 140 (2019) 513-538 | https://doi.org/10.1016/j.renene.2019.03.088 |
| 6 | L.P. Singh, D. Ali, I. Tyagi, U. Sharma, R. Singh, P. Hou | Durability studies of nano-engineered fly ash concrete | 2019 | Construction and Building Materials 194 (2019) 205-215 | https://doi.org/10.1016/j.conbuildmat.2018.11.022 |

| | Author(s) | Title | Year | Journal | DOI Number or URL |
|---|---|---|---|---|---|
| **7** | Amal Abdelhaleem, Wei Chu, Xiaoliang Liang | Diphenamid degradation via sulfite activation under visible LED using $Fe^{+3}$ impregnated N-doped $TiO_2$ photocatalyst | 2019 | Applied Catalysis B: Environmental Volume 244, 5 May 2019, Pages 823-835 | https://doi.org/10.1016/j.apcatb.2018.11.085 |
| **8** | Yonathan Reches | Nanoparticles as concrete additives: Review and Perspectives | 2018 | Construction and Building Materials 175 (2018) 483-495 | https://doi.org/10.1016/j.conbuildmat.2018.04.214 |
| **9** | L.D. García, J.M. Pastora, J. Peña | Self-cleaning and depolluting glass reinforced concrete panels: Fabrication, optimization and durability evaluation | 2018 | Construction and Building Materials Volume 162, 20 February 2018, Pages 9-19 | https://doi.org/10.1016/j.conbuildmat.2017.11.156 |
| **10** | Maria Kaszynska, and Norbert Olczyk | The Influence Of $TiO_2$ Nanoparticles on the Properties of Self-Cleaning Cement Mortar | 2018 | | https://doi.org/10.5593/sgem2018/6.3 |
| **11** | Jing Li, Danzhen Zhang, Tingting Yang Shen Yang, Xudong Yang, Hongwei Zhu | Nanofibrous membrane of graphene oxide-in-polyacrylonitrile composite with low filtration resistance for the effective capture of PM2.5 | 2018 | Journal of Membrane Science 551 (2018) 85-92 | https://doi.org/10.1016/j.memsci.2018.01.025 |
| **12** | J. Nayak, A.K. Mohapatra, and H. Kim | Effects of Surface Carbon on the Visible-light Photocatalytic Activity of Nitrogen Doped $TiO_2$-C Nanocomposite Powder | 2018 | Current Nanoscience, 2016, 12, 365-371 | |
| **13** | Aiqin Mao, Peipei Ding, Feng Quan, Tianchi Zhang, Xueqin Ran, Yibu Li, Xia Jin, Xiaolong Gu | Effect of aluminum element on microstructure evolution and properties of multicomponent Al-Co-Cr-Cu-Fe-Ni nanoparticles | 2018 | Journal of Alloys and Compounds Volume 735, 25 February 2018, Pages 1167-1175 | https://doi.org/10.1016/j.jallcom.2017.11.233 |

| | Author(s) | Title | Year | Journal | DOI Number or URL |
|---|---|---|---|---|---|
| **14** | Young Kyu Kim, Seong Jae Hong, Hyung Bae Kim, and Seung Woo Lee | Evaluation of In-Situ $NO_x$ Removal Efficiency of Photocatalytic Concrete in Expressways | 2018 | KSCE Journal of Civil Engineering (2018) 22(7):2274-2280 | 10.1007/s12205-017-0028-9 |
| **15** | Seunghyun Weon, Eunji Choi, Hyejin Kim, Jee Yeon Kim, Hee-Jin Park, Sae-mi Kim, Wooyul Kim, and Wonyong Choi | Active Facet Exposed $TiO_2$ Nanotubes Photocatalyst Filter for Volatile Organic Compounds Removal: From Material Development to Commercial Indoor Air Cleaner Application | 2018 | Environmental Science and Technology2018, 52 9330-9340 | |
| **16** | Adriana C. Mera, A. Martínez-de la Cruz, E. Pérez-Tijerina, M.F. Meléndrez, Héctor Valdése | Nanostructured BiOI for air pollution control: Microwave-assisted synthesis, characterization and photocatalytic activity toward NO transformation under visible light irradiation | 2018 | Materials Science in Semiconductor Processing Volume 88, December 2018, Pages 20-27 | https://doi.org/10.1016/j.mssp.2018.04.045 |
| **17** | Zhen Lenga, Huayang Yu, Zheming Gao | Study on air-purifying performance of asphalt mixture specimens coated with titanium dioxide using different methods | 2018 | International Journal of Pavement Research and Technology xxx (2018) | https://doi.org/10.1016/j.ijprt.2018.08.003 |
| **18** | Zu Wen and Dehong Xia | A thermodynamics model for morphology prediction of aluminum nano crystals fabricated by the inert gas condensation method | 2018 | Nanotechnology 29, 125301 | https://doi.org/10.1088/1361-6528/aaa84d |
| **19** | Maria Kaszynska, Norbert Olczyk | The Influence of $TiO_2$ Nanoparticles on the Properties of Self-Cleaning Cement Mortar | 2018 | Section Green Buildings Technologies and Materials | https://doi.org/10.5593/sgem2018/6.3 |

| | Author(s) | Title | Year | Journal | DOI Number or URL |
|---|---|---|---|---|---|
| **20** | Peng Zhang, Dongyang Wan, Zhenyi Zhang, Guodong Wang, Junhua Hu, Guosheng Shao | RGO-functionalized polymer nanofibrous membrane with exceptional surface activity and ultra-low airflow resistance for PM 2.5 filtration | 2018 | Environ. Sci.: Nano, (2018) 5, 1813 | https://doi.org/10.1039/c8en00468d |
| **21** | Xiao Chen, Zhenglong Zhao, Ying Zhou, Qiulian Zhu, Zhiyan Pana, Hanfeng Lu | A facile route for spraying preparation of Pt/$TiO_2$ monolithic catalysts toward VOCs combustion | 2018 | Applied Catalysis A: General Volume 566, 25 September 2018, Pages 190-199 | https://doi.org/10.1016/j.apcata.2018.08.025 |
| **22** | Vinita Vishwakarma, and D. Ramachandran | Green concrete mix using sold waste and nanoparticles as alternatives—A review | 2018 | Construction and Building Materials 162 (2018) 96-103 | https://doi.org/10.1016/j.conbuildmat.2017.11.174 |
| **23** | Thomas A.J Kuhlbusch, Susan W.P Wijnhoven, and Andrea Haase | Nanomaterial exposures for worker, consumer and the general public | 2018 | NanoImpact 10 (2018) 11-25 | |
| **24** | Rodolphe Carpentier, Anne Platel, Helena Maiz-Gregores, Fabrice Nesslany, and Didier Betbeder | Vectorization by nanoparticles decreases the overall toxicity of airborne pollutants | 2018 | PLoS ONE 12 (8) e0183243 | https://doi.org/10.1371/journal.pone.0183243 |
| **25** | Xiaohui Tang, Jean-Pierre Raskin, Driss Lahem, Arnaud Krumpmann, André Decroly, and Marc Debliquy | A Formaldehyde Sensor Based on Molecularly-Imprinted Polymer on a $TiO_2$ Nanotube Array | 2017 | Sensors2017,17, 675; | https://doi.org/10.3390/s17040675 |
| **26** | Boris Mahltig and Haoqian Miao | Microwave-assisted preparation of photoactive $TiO_2$ on textile substrates | 2017 | J. Coat. Technol. Res.,14(3) 721–733, 2017 | https://doi.org/10.1007/s11998-016-9891- 4 |

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| **27** | Yanjia Yu, Junmin Wana, Ziang Yang, and Zhiwen Hu | Preparation of the $MoS_2/TiO_2$/HMFs ternary composite hollow microfibres with enhanced photocatalytic performance under visible light | 2017 | Journal of Colloid and Interface Science Volume 502, 15 September 2017, Pages 100-111 | https://doi.org/10.1016/j.jcis.2017.04.058 |
| **28** | N.B. Singh, Meenu Kalra, and S.K. Saxena | Nanoscience of cement and concrete | 2017 | Materials Today: Proceedings 4 (20147) 5478-5487 | |
| **29** | Hossein Mohammadhosseini, Jamaludin Mohamad Yatim, Abdul Rahman Modh Sam, and A.S.M Abdul Awal | Durability performance of green concrete composites containing waste carpet fibers and palm oil fuel ash | 2017 | Journal of Cleaner Production 144 (2017) 448-458 | |
| **30** | M.S. Muhd Norhasri, M.S. Hamidah, and A Mohd Fadzil | Applications of using nano materials in concrete: A review | 2017 | Construction and Building Materials 133 (2017) 91-97 | http://dx.doi.org/10.1016/j.conbuildmat.2016.12.005 |
| **31** | Shen Yang, Zhenxing Shu, Fei Wei, and Xudong Yang | Carbon nanotubes/activated carbon fiber-based air filter media for simultaneous removal of particulate matter and ozone | 2017 | Building and Environment 125 (2017) 60-66 | http://dx.doi.org/10.1016/j.buildenv.2017.08.040 |
| **32** | Anwar M. Mohamed | Influence of nano materials on flexural behavior and compressive strength of concrete | 2016 | HBRC Journal (2016) 12, 212-225 | http://dx.doi.org/10.1016/j.hbrcj.2014.11.006 |
| **33** | Marisol Faraldos and Ana Bahamonde | Environmental applications of titania-graphene photo catalysts | 2017 | Catalysis Today 285 (2017) 13-28 | http://dx.doi.org/10.1016/j.cattod.2017.01.029 |
| **34** | N.B. Singh, Meenu Kalra, and S.K. Saxena | Nanoscience of Cement and Concrete | 2017 | Materials Today: Proceedings 4 (2017) 5478–5487 | |

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| **37** | J Nayak, A. K. Mohapatra, and H. Kim | Effects of Surface Carbon on the Visible-light Photocatalytic Activity of Nitrogen Doped $TiO_2$-C Nanocomposite Powder | 2016 | Current Nanoscience 12 (2016) 365-371 | |
| **38** | Giampiccolo, Andrea; Ansell, Martin; Tobaldi, David; & Ball, Richard | Synthesis of Co–TiO2 nanostructured photocatalytic coatings for MDF substrates | 2016 | Institution of Civil Engineers: Green Materials, vol. 4, no. 4, pp. 1-10. | https://doi.org/10.1680/jgrma.16.00004 |
| **39** | Ataallah Nadiri, Marwa M. Hassan, and Somayeh Asadi | Supervised Intelligence Committee Machine to Evaluate Field Performance of Photocatalytic Asphalt Pavement for Ambient Air Purification | 2015 | Transportation Research Record: Journal of the Transportation Research Board, No. 2528, Transportation Research Board, Washington, D.C., 2015, pp. 96–105. | https://doi.org/10.3141/2528-11 |

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| **40** | Jiaqiang Wang, Encai Ou, Junjie Li, Xiaoyun Yang, Wei Wang, Zhiying Yann, and Cong Li | Synthesis of mesoporous titania–graphite composite emplated by hypocrellins for visible-light photocatalytic degradation of acetaldehyde | 2015 | Materials Science in Semiconductor Processing Volume 31, March 2015, Pages 397-404 | https://doi.org/10.1016/j.mssp.2014.12.029 |
| **41** | Sammy W. Verbruggen | $TiO_2$ photo catalysis for the degradation of pollutants in gas phase: From morphological design to plasmonic enhancement | 2015 | Journal of Photochemistry C: Photochemistry Reviews 24 (2015) 64-82 | ttp://dx.doi.org/10.1016/j.jphotochemrev.2015.07.001 |
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**Table A2: Journal Items on Non-Nano Techniques for Emissions Reduction**

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