

Heterogeneous Photocatalysts Based on TiO₂ for Abatement of Hazardous Air Pollutants

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Abstract

A mixture of suspended solid particles and gases coming from car emissions, chemicals from factories, dust, and pollen in the air is called air pollution. Human exposure to common hazardous air pollutants such as NO_x, SO_x, CO, H₂S, NH₃, and VOCs is associated with chronic respiratory diseases and cancer. Moreover, exposure to one of the most dangerous forms of air pollution very fine particulates PM_{2.5} can cause such deadly illnesses as lung cancer, stroke, and heart disease. Given all these facts, this paper discusses newly developed advanced smart building materials based on TiO₂ with self-cleaning and pollutant removal capability from the environment.

Keywords: Photocatalysis; TiO₂; Nanomaterials; Air pollutants; SO_x; NO_x; VOC

Introduction

People take thousands of breaths daily, leading to a total intake of about 10,000 liters of air per day. Consequently, the lung receives significant doses of many air contaminants, even those present at seemingly low and trivial concentrations [1].

Air pollution is a mixture of solid particles and gases in the air. Car emissions, chemicals from factories, dust, pollen, and mold spores may be suspended as particles. Air pollution is a familiar environmental health hazard. Air pollution was regarded primarily as a threat to respiratory health. Air pollution exposure is associated with oxidative stress and inflammation in human cells, which may lay a foundation for chronic diseases and cancer. In 2013, the International Agency for Research on Cancer of the World Health Organization (WHO) classified air pollution as a human carcinogen [1].

Nowadays and many years before, the most energy worldwide is provided by fossil fuel which combustion leads to severe pollution and contributes to the greenhouse effect. This obviously applies to power plants but also to many other industrial activities that may have their own onsite electricity or heat production, such as iron and steel manufacturing or cement production. Some activities generate dust that contributes to particulate matter concentrations in the air, whereas solvent use, for example in metal processing or chemical production, may lead to emissions of polluting organic compounds.

Climate is a main driver for hydrogen in the energy transition. Limiting global warming to below 2 degrees Celsius (°C) requires that CO₂ emissions decline by around 25% by 2030, from 2010 levels, and reach net zero by around 2070 [2]. For a reasonable likelihood to stay below 1.5 °C of warming, global net anthropogenic CO₂ emissions should decline by around 45% by 2030, from 2010 levels, reaching net-zero by around 2050. Hydrogen is the most ideal alternative to clean energy, but currently, there is no significant hydrogen production from renewable sources [3].

Hazardous air pollutants are those known to cause cancer and other serious health impacts. Common hazardous compounds include NO_x, SO_x, CO, H₂S, NH₃, other nitrogen compounds (e.g., hydrogen cyanide), sulfur-containing compounds (organothiols), hydrocarbons, and a myriad of volatile organic compounds (VOCs) (benzene, toluene, methanol, etc.) which are of significant concern for environmental remediation [4]. In the class of aromatic compounds, polycyclic aromatic hydrocarbons (PAHs) are mostly colourless, white, or pale yellow solids.

They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. PAHs are commonly detected in air, soil, and water [5].

One of the most dangerous forms of air pollution are very fine particulates capable of penetrating deep into the lungs and entering the bloodstream. Known as $PM_{2.5}$, these particulates have an aerodynamic diameter of less than 2.5 microns - about one-thirtieth the width of a human hair. Exposure to $PM_{2.5}$ can cause such deadly illnesses as lung cancer, stroke, and heart disease.

According to the 2019 World Air Quality Report [6], it is estimated to contribute toward 7 million premature deaths a year, while 92% of the world's population are estimated to breathe toxic air quality [7]. In less developed countries, 98% of children under five breathe toxic air. As a result, air pollution is the main cause of death for children under the age of 15, killing 600,000 every year [8]. In financial terms, premature deaths due to air pollution cost about \$5 trillion in welfare losses worldwide [9]. Using a weighted population average, Bangladesh emerges as the most polluted country for $PM_{2.5}$ fine particulate matter exposure, based on available data. Pakistan, Mongolia, Afghanistan and India follow behind respectively, deviating from one another by less than 10%. Bosnia and Herzegovina is the highest-ranking country in Europe for $PM_{2.5}$ pollution, featuring as the 14th most polluted country globally, with only $4\mu\text{g}/\text{m}^3$ less than China's national $PM_{2.5}$ weighted average.

Air emissions from industry in Europe have decreased over recent years. Between 2007 and 2017, overall emissions of sulphur oxides (SO_x) declined by 54%, nitrogen oxides (NO_x) by more than

one-third and greenhouse gases from industry, including power plants, by 12% [10].

Using data from Sentinel 5-P satellite shows that in lockdown areas, average NO_2 levels in 2020 for the period March 15 to April 30 were lower than levels in 2019. These results were expected as vehicular traffic, one of the main sources of NO_2 emissions was dramatically reduced during the lockdown [11]. Recently, has been discussed about the successful implementation of nanomaterials for the purification of air in automotive exhaust systems and petroleum refining systems with greater efficiency than conventional techniques [12].

Actually, nanotechnology is an interdisciplinary study that allows us to develop new materials with new, interesting, and useful properties. Especially, photocatalytic degradation techniques should be more used in air purification because with this technique it is possible to decrease pollutants to certain acceptable limits [13].

Photocatalysis is a promising technology for air purification because it can decompose gaseous pollutants (particularly volatile organic compounds (VOCs) directly into harmless CO_2 and H_2O under ambient conditions. Photocatalysis can be particularly suitable for removing low concentration pollutants (sub-ppm levels) in indoor environments where conventional adsorption technologies are not very efficient. Although photocatalytic air purification has been extensively investigated, it still falls far short of satisfying the requirements for practical usage [14]. However, there are challenges with regards to photocatalytic efficiency improvements, lab to industrial scaling up, and commercial product production. Figure 1 schematically shows the problems of air pollution and possible photocatalytic solutions based on TiO_2 .

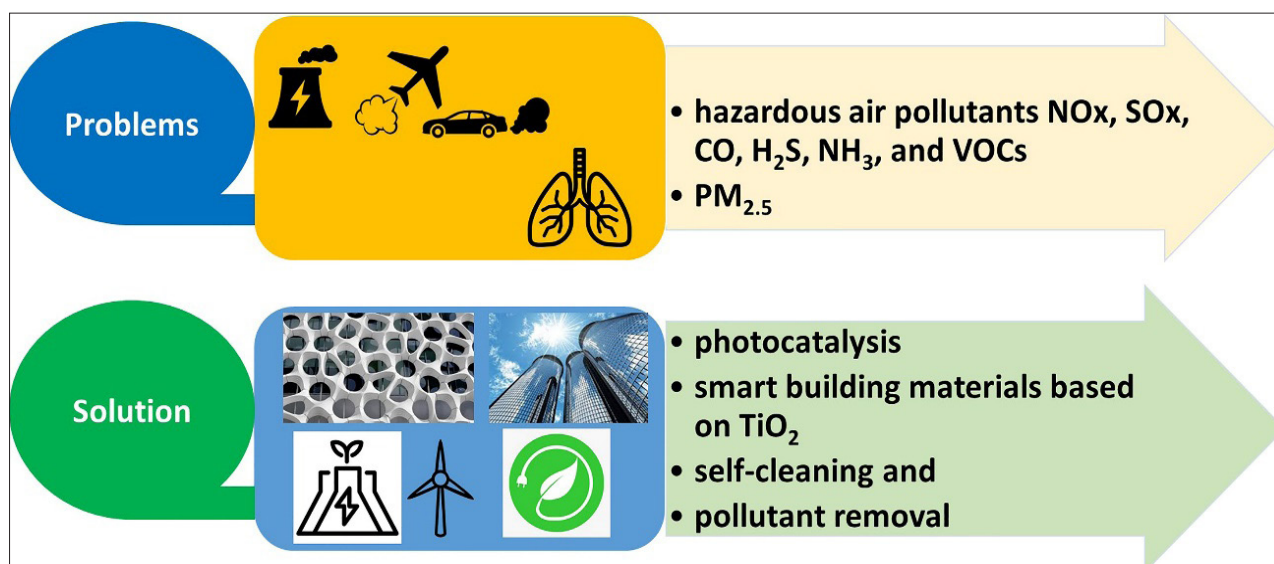


Figure 1: The problems of air pollution and possible photocatalytic solutions based on TiO_2 .

In recent years, a number of products based on the photocatalytic properties of a thin layer of TiO_2 at the surface of the material (such as glass, pavement, etc.) or embedded in paints

or concrete have been used as photocatalytic self-cleaning and “depolluting” materials as a remediation technology mainly for NO_x and aromatic VOCs in urban areas. The use of TiO_2 photocatalysts

as an emerging air pollution control technology has been reported in many locations worldwide. However, up to now, the effectiveness measured in situ and the expected positive impact on air quality of this relatively new technology has only been demonstrated in a limited manner [15].

Air pollutants

Air pollutants can be classified according to their origin as primary or secondary pollutants. Primary pollutants are those that are emitted directly by the sources to the atmosphere, like carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen oxides (NO_x) and particles (PM₁₀ and PM_{2.5}). Secondary pollutants are formed from chemical reactions occurring in atmosphere, such as tropospheric ozone (O₃), nitric acid (HNO₃) and sulfuric acid (H₂SO₄) [16]. Ozone (smog) is created when pollutants emitted by cars, power plants, industrial boilers, refineries, and other sources chemically react in the presence of sunlight. Chemical interactions between SO_x and NO_x can produce ground-level ozone, and this can happen in the upper atmosphere too, leading to photochemical smog and acid rain [17].

The major source of NO_x in Europe is road transport, producing around 40% of the total emissions, comprising a mixture of nitric oxide (NO) and nitrogen dioxide (NO₂) [18]. Gaseous pollutants are mainly controlled or removed by a few significant techniques: absorption, adsorption, chemical oxidation, and incineration. These techniques may be employed either singly or in combination, which, in turn, can be decided based on the type of pollutant. Gas adsorption is a surface phenomenon where gas molecules are adsorbed or are attracted to the surface and held on the surface of the solid.

Heterogeneous photocatalysts for abatement of air pollutants

The photocatalytic process is usually performed at room temperature and atmospheric pressure, and the possibility of using natural resources as sunlight, the morphology modification of the photocatalyst, makes easier the separation and reuse steps of the catalyst. Photocatalytic nanoparticles are able to promote the degradation of pollutants in aqueous and gas matrices, with resulting products presenting a lower environmental impact [19].

Titanium dioxide considered as one of the most environmentally friendly active photocatalysts that can be used with building materials safely and effectively to react with nitric oxides. TiO₂ is frequently used to oxidize organic and inorganic compounds in air and water due to its strong oxidative ability and long-term photostability [20]. TiO₂ is also a very common, non-expensive, and non-toxic material [21].

When TiO₂ nanoparticles are stimulated by sunlight, they convert air pollutants such as nitrogen oxides (NO_x), volatile organic compounds (VOCs), carbon monoxide (CO), and ozone to more environmentally acceptable products such as calcium nitrate and carbon dioxide. Recently, Gopalan and co-workers summarized

the prospective applications of TiO₂-based building materials (cement, mortar, concretes, paints, coating, etc.) with relevance to the removal of outdoor/indoor NO_x and volatile organic compounds, self-cleaning of the surfaces, etc. [22]. Already in 1999 Chiba of Japan [23] and Milan of Italy in 2002 [24] have applied the nano-TiO₂ in the construction of cement concrete pavement. Also, it has been reported the use of TiO₂ as a stone coating for self-cleaning and biocidal purposes for the protection of buildings and cultural heritage [25,26].

TiO₂ for NO_x degradation

The mechanism for photocatalytic NO_x removal involves the adsorption of NO₂ gas molecules onto hardened cement paste structures, the occurrence of hydrolysis of NO₂ into the pores, and the formation of soluble nitrates [27].

These experimental results demonstrated that cementitious materials could be tailored to decrease NO_x levels through photocatalysis and showed their ability to bind NO_x, in particular, NO₂. Paved surfaces (e.g., highways, runways, parking lots, etc.) generally account for up to ~60% of developed urban areas and could be modified with a thin layer of TiO₂-inclusive photocatalytic materials so that the topmost surface effectively clears the environment of the adverse effects of pollutants coupled through the influence of solar reflectance. In addition, urban temperatures could be controlled by simply coating wall surfaces with white photocatalytic materials. Such applications can be extended to parking lots and roads to reduce temperatures and to cool the environment, as well as to improve air quality Gopalan et al. [22].

Recently Huanan et al. 2020 evaluated nano-TiO₂ as a coating material for both road surface and roadside for NO_x degradation. The nano-TiO₂ coating materials were prepared by using anatase nano-TiO₂, activated carbon powder, silane coupling agent, and deionized water. The results show that the material has good photocatalytic degradation performance, and the proper amount of silane coupling agent can enhance the bonding performance of the material and asphalt mixture. For the roadside coating, sodium dodecylbenzene sulfonate was selected as the surfactant to carry out the photocatalytic degradation experiment of NO₂ with different dosages of surfactant. The results showed that when the mass ratio of nano-TiO₂ and surfactant was about 1:2, the catalytic degradation effect of the material was the best [28]. Hussein et al. [29] prepared two types of substrates coatings containing TiO₂. First, mixing nanoparticles of TiO₂ with cement paste in 3% and 6% percent. Second, mortar substrates coated with nano TiO₂ aqueous solution. Two coating methods have been used dip and spray. They tested its efficiency in NO gas removal. Results showed the effectivity of coating building materials with titanium dioxide, the removal of gaseous pollutants like nitric oxide reached to 98.85% when spray and dip methods are used. Mixing nano titanium with a percent of 3% was also efficient in the removal of nitric oxides, the removal reached 97%. The research has shown that the spray method was more practical to be used.

TiO₂ for SO_x degradation

Titanium dioxide (TiO₂) has been used in building materials to produce products that do not require major maintenance and contribute to improve air quality and extend the life of buildings. Thus, Fernandes and co-workers (2020) [30] developed mortars at a weight ratio of 1:3 (cement: sand), incorporating 2.5%, 5%, 7.5%, and 10% of TiO₂ relative to the cement weight. They studied prepared materials in process of degradation of sulphur dioxide (SO₂), as one of the largest atmospheric pollutants. The samples were exposed to an accelerated aging SO₂ (pollutant) chamber, then moistened and exposed to ultraviolet radiation. For this exposure of the samples, two Light Emitter Diodes (LEDs) with wavelengths covering the UV-A range were used: UV (380-420nm) and blue (420-493nm). The results have shown that the incorporation of TiO₂ improved the physical, mechanical and photocatalytic properties, and enabled the decontamination of mortars due to the action of the SO₂ pollutant.

Mostafa et al. [31] have prepared active photocatalytic nanostructures to harvest the abundant sunlight energy for clean energy production and environmental management. Different calcium carbonate-titania nanostructures were applied as novel photocatalysts for desulfurization of dibenzothiophene (DBT) and gas oil using different radiation sources at room temperature. The results have shown that 95% desulfurization of DBT was possible under 1h visible light irradiation with linear halogen lamp (LHL) at catalyst/DBT-solution = 10g/L, while ultra-clean diesel production (99% removal, 3.47ppm) could be obtained via normal sunlight photochemical desulfurization of diesel fuel by calcium carbonate titania photocatalyst in presence of H₂O₂ and acetic acid as oxidizing agents and acetonitrile as a solvent. The prepared calcium titanate photocatalysts have bandgap energy (2.05eV), and stable photocatalytic activity with enhanced visible light removal of organosulfur compounds for economic ultra-clean fuel production, pollution control, and environmental management.

TiO₂ for VOC degradation

One of the major drawbacks of photocatalysis in the gaseous phase (the reactions occurring at the gas-solid interface) during VOC degradation is rapid loss of photocatalytic activity during prolonged irradiation and repeated uses because of either the intrinsic instability of the materials or the fouling of the photocatalyst surface [32].

During the Photocatalytic Degradation (PCD) of VOCs, degradation intermediates are formed on the surface of the photocatalyst and some of them are often more strongly complexed with the photocatalyst than the parent substrate molecules. The accumulation of the recalcitrant intermediates onto the catalyst surface not only blocks light to inhibit photon absorption but also limits the diffusion of dioxygen or other target compounds onto the active sites. As a result, the accumulation of recalcitrant carbon deposits on the surface eventually deactivates the photocatalysts [14].

For example, Einaga et al. [33] reported that the PCD efficiency of aromatic VOCs is markedly reduced after 2h of photoreaction: 63% to 9% for toluene, 38% to 9% for benzene, 41% to 28% for cyclohexene, and 66% to 57% for cyclohexane [33].

Conclusion

Still, vast populations around the world lack access to air quality information. Often these areas are estimated to have some of the world's most severe air pollution, putting the health of huge populations at risk. More monitoring data is needed to bridge the information gap and better tackle air pollution globally.

The development of advanced building materials based on TiO₂ offers additional novel functionalities (such as self-cleaning, pollutant removal capability) with new technologies in both residential and commercial buildings, in the process of developing smarter, more energy-efficient, and more secure infrastructures that will address environmental and global social challenges. In this regard, scientific developments in modern material synthesis and nanotechnology provide an adequate platform for the design and creation of new and smart building materials with tailored properties.

Conflict of Interest

There are no conflicts to declare.

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