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# Fighting global warming: the potential of photocatalysis against $CO_2$, $CH_4$, $N_2O$, CFCs, tropospheric $O_3$, BC and other major contributors to climate change.

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## ABSTRACT

At the laboratory scale, photocatalysis is a promising method to convert many air pollutants such as nitrogen oxides and volatile organic compounds, to safer products for human health but also environmentally more acceptable, such as nitrate and carbon dioxide.

Indoor and industrial applications of photocatalysis to remove local air pollutants from the atmosphere are now numerous. Large scale outdoor applications of photocatalysis started with self-cleaning glass, coatings and paints for buildings, and several outdoor experiments have been documented regarding the photocatalytic reduction of NOx levels in urban environment, such as tunnels, streets and highways.

The potential applications of photocatalysis to remove or mitigate a wide range of global warming contributors from the atmosphere seems an attractive method to help fighting climate change. By harnessing solar energy, photocatalytic processes consume less energy than conventional methods. This review article shows that photocatalysis may be applied successfully to eliminate or transform of all major long-lived well mixed greenhouse gases, but also soot and tropospheric ozone and other short-lived climate forcers. The cases of sulphur hexafluoride and nitrogen trifluoride are also discussed.

KEYWORDS: photocatalysis; greenhouse gases removal; climate forcers elimination; global warming reduction.

# 1. INTRODUCTION

According to reference scenario projections or the 'business as usual' scenario from the International Energy Agency (IEA), to meet the needs of populations in 2030, the world will need over 55% more primary energy than in 2005, with an increase in global carbon dioxide ($CO_2$) emissions of 57%.

Scientific studies on photocatalysis started about four decades ago. One of the most basic materials in our daily life, titanium dioxide ($TiO_2$) has emerged as an excellent photocatalytic material for environmental purification.

Advances in photocatalysis science and technology, as well as in industrial applications, point out the promising potential of photocatalysis for reducing the levels of greenhouse gases (GHG) in the atmosphere, with a positive impact on climate change effects.

In 2003, Centi [1]reviewed the catalytic technologies for the abatement of greenhouse gases, which focused on the elimination of nitrous oxide ($N_2O$) and methane ($CH_4$) and in the conversion of $CO_2$ by thermal catalysis.

This paper focuses on photocatalytic technologies at room temperature to eliminate not only $N_2O$, $CH_4$ and $CO_2$ but also all the other major contributors to global warming: black carbon (BC), chlorofluorocarbons (CFCs), tropospheric ozone ($O_3$) and its precursors: volatile organic compounds (VOC), nitrogen oxides (NOx), and some other GHGs or short-lived climate forcers.

### 1.1. Principle of photocatalysis

Photocatalytic reactions [2] use the energy of photons from light sources to activate a catalyst.

Upon activation, adsorbed gases, particularly molecular oxygen ($O_2$), or hydroxide radical ($OH^{\cdot}$) and contaminant species (organic or mineral compounds), can participate in surface-mediated reactions that, under appropriate operating conditions, can produce and desorb product species, notably $CO_2$ and $H_2O$.

A photocatalytic reaction generally includes the following processes: when photons have a higher energy than the semiconductor band gap, they are absorbed, and electrons in the valence band are promoted to the conduction band, leaving positive holes in the valence band. The excited electron is used to reduce substances, while the positive hole is used to oxidize substances on the surface of the photocatalyst. Importantly, by modulating the Red-Ox potential of a photocatalyst, selectivity may be obtained to conduct reduction reactions, oxidation partial oxidation reactions and many researches are focused on that goal.

Since the discovery by Fujishima and Honda in 1972 [3]of the photocatalytic splitting of water on a $TiO_2$ electrode under ultraviolet (UV) light, enormous research efforts have been devoted to photocatalysis under UV light in the presence of many semiconductors and semiconductor oxides [4] such as $TiO_2$, CdS, $SnO_2$, $WO_3$, $SiO_2$, $ZrO_2$, ZnO, $Nb_2O_3$, $Fe_2O_3$, $SrTiO_3$,, $CeO_2$, $Sb_2O_4$, $V_2O_5$... and this topic developed very quickly during the last twenty five years.

In the past years, visible light photocatalysis has gained considerable attention, allowing a better use of sunlight spectrum (i.e. 40 – 50 % instead of 4-5% for UV). Researches on photocatalytic methods, while still in progress, have led to many promising applications for environmental purposes. Still many aspects remain to be solved like: photocatalytic efficiency improvement, increased solar energy utilization, suitable form of catalyst, all in turn influencing the economic aspects of this technique.

This review article will first describe the potential of photocatalysis against all major long-lived well mixed greenhouse gases (LLGHGs). Then, the potential of photocatalysis against the principal short-lived climate forcers (SLCFs) will be discussed. A third part will be dedicated to large-scale indoor air photocatalytic treatments and outdoor applications of photocatalysis to clean off atmospheric environment.

## 2. PART 1: The potential of photocatalysis against $CO_2$, $CH_4$, $N_2O$ and CFCs

The well-mixed long-lived greenhouse gases: $CO_2$, $CH_4$, $N_2O$, CFCs, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride ($SF_6$) are collectively referred as the LLGHGs. Radiative forcing (RF) is a concept used for quantitative comparisons of the strength of different human and natural agents in causing climate change. According to the National Oceanic and Atmospheric Administration (NOAA) [5], the first five major LLGHGs ($CO_2$, $CH_4$, $N_2O$, CFC-12 and CFC-11) account for about 96% of the direct radiative forcing since 1750.

In table 1 the main characteristics of LLGHGs are listed in terms of Global Radiative Forcing in $W.m^{-2}$, Global Warming Potential $GWP_{100}$ (time horizon of 100 years), Atmospheric lifetimes in years and relative importance in %.

*Insert table 1*

## 2.1. Photocatalytic reduction of carbon dioxide

Carbon dioxide has increased in the atmosphere from fossil fuel use in industry and transportation, manufacture of cement, building air conditioning and deforestation.

With a global radiative forcing of 1.74 $W.m^{-2}$, $CO_2$ is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63% of the total.

This chapter addresses the potential application of photocatalysis to recycle $CO_2$ in valued chemicals by photocatalytic reduction, also called 'artificial photosynthesis'. The reaction scheme is the following:

$CO_2 + H_2O$ (hυ / photocatalyst) → Carbonaceous products + $O_2$

During the 70's and the 80's the electrocatalytic reduction of $CO_2$ has been investigated, for instance by Fisher [6]. Then the photo-electrocatalytic reduction of $CO_2$ on semiconductors started to be studied [7].

In 1987, Thampi, Kiwi and Graetzel [8] reported the photo-methanation of $CO_2$ at room temperature and atmospheric pressure using dispersed ruthenium and ruthenium oxides loaded onto $TiO_2$. Quickly after, many other research teams described photocatalytic reduction of $CO_2$ with $H_2O$ on various $TiO_2$ catalysts at room temperature, producing methanol ($CH_3OH$) and carbon monoxide (CO) (Anpo [9,10] ) or over a cerium oxide

$CeO_2$ - $TiO_2$ photocatalyst irradiated by visible light, in which reaction products were hydrogen and methane (Ogura [11]).

Several articles (Usubharatana [12], Roy [13]) have reviewed all types of photocatalysts used for photo-reduction of $CO_2$, meanwhile Kočí [14] has provided an overview of the literature data from 1994 till 2007 regarding $CO_2$ photocatalysis in the presence of $TiO_2$. The most widely employed catalyst is $TiO_2$ and the reaction products are generally methane, or methanol. However, the photocatalytic conversion of $CO_2$ has been studied with many types of catalysts, and the main $CO_2$ reduction photocatalysts are listed in table 2.

***Insert table 2***

Recently, Wang [15] studied visible light photo-reduction of $CO_2$ using CdSe/Pt/$TiO_2$ catalysts; Varghese [16] described high rate solar photocatalytic conversion of $CO_2$ and water vapour to hydrocarbon fuels; Nasution [17] performed the synthesis of methanol from $CO_2$ by photocatalytic reduction over copper-doped $TiO_2$ and Zhang [18] selectively produced $CH_4$ from $CO_2$ on Pt-loaded $TiO_2$ photo-catalyst.

Kočí [19] studied the effect of temperature, pressure and volume of reactant solution on the photocatalytic reduction of $CO_2$ over suspended $TiO_2$ in an annular batch photoreactor. These same parameters were also examined in the reviews previously cited. In most cases, $CO_2$ reduction is conducted over $TiO_2$ with water or water vapour as the reducing agent.

Several other review articles on the photocatalytic reduction of $CO_2$ have been published (Indrakanti [20], Anpo [21]), as well as by other methods [22,23]. Although the irradiation wavelength and many other parameters are not yet optimized, the different photocatalytic processes cited herein can help remove $CO_2$ from the atmosphere, but they can also convert $CO_2$ into some useful chemicals including $CH_4$, $H_2$, CO, $CH_3OH$, formaldehyde, ethanol, higher hydrocarbons, etc. providing a carbon-neutral energy alternative to fossil fuels. Improvements in the photo-efficiency of photocatalysts used in these reactions are still needed to prove its feasibility.

Grills [24] explored new directions for the photocatalytic reduction of $CO_2$ by supramolecular or biphasic ionic liquid supercritical $CO_2$ systems.

### 2.2. Photocatalytic oxidation of methane

Methane has increased in the atmosphere as a result of human activities related to agriculture, natural gas distribution and landfills. The concentration of $CH_4$ in the atmosphere has almost tripled in the last 150 years. Current natural and man-made sources include coal mining but also fermentation sources from ruminant livestock, rice cultivation, landfill, wastewater, wetlands and marine sediments.

Methane is a powerful GHG responsible for nearly one-fifth of anthropogenic global warming with a global radiative forcing of 0.50 $W.m^{-2}$, representing 18.2% of the total among the LLGHGs in 2008.

Per kilogram, $CH_4$ is 25 times more powerful than $CO_2$ over a 100-year time horizon ($GWP_{100}$=25) and global warming is likely to enhance methane release from a number of sources (including permafrost and submarine methane hydrates). Transforming atmospheric $CH_4$ into equimolar amounts of $CO_2$ can have a significant impact on reducing global warming. Recently Boucher [25] suggested atmospheric methane removal as a way to mitigate climate change, meanwhile Bastviken [26] compiled $CH_4$ emission estimates from 474 freshwaters and found them to be, expressed in $CO_2$ equivalents, 25% of the estimated total terrestrial GHG sink.

This chapter reviews the complete oxidation of trace levels of GHG methane present in the atmosphere into $CO_2$ and $H_2O$ according to the reaction scheme:

$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$

Table 3 summarizes some research on the photocatalytic oxidation of methane and/or other low molecular weight alkanes under UV.

***Insert table 3***

Pioneer work was conducted in 1972 - 1974 by Fromenti, Teichner and Djeghri as they described the photo-oxidation of linear and branched alkanes, from ethane to octane (C2 to C8), at room temperature, on the surface of anatase particles of $TiO_2$, under ultra-violet illumination (210–390 nm).

Although some authors like Kaliaguine [30] used a vanadium derivative ($V^{5+}/SiO_2$) as well as $TiO_2$, very often authors used $TiO_2$ based photocatalysts, [36-39,41-43] and investigated the kinetics of the total oxidation of methane, ethane, ethene and propene using $TiO_2$. Others like Krishna [40] demonstrated the high activity of an uranyl derivative as an heterogeneous photocatalyst for the total oxidation of $CH_4$ at room temperature under ambient sunlight conditions. No partial oxidation products such as carbon monoxide, methanol, formaldehyde, and formic acid were formed.

Wataru [45] studied the photocatalytic decomposition of chlorodifluoromethane, methane and tetrachloromethane over $TiO_2$ because these compounds have the same structure but different constituents. The decomposition rate was found to be the highest for $CHClF_2$, followed by $CH_4$ and $CCl_4$ in decreasing order and reactions were first-order within the concentration range used. The activation energies obtained from the overall reaction rate constants were 13.7 $kJ.mol^{-1}$ for $CHClF_2$, 16.6 $kJ.mol^{-1}$ for $CH_4$ and 66.1 $kJ.mol^{-1}$ for $CCl_4$.

Almost all the cited work in table 3 was conducted at the laboratory scale but several publications mentioned $CH_4$ photo-elimination in an open space, or at a larger scale (Espagnol [48], Guarino [50], Costa [51]). In part 3 of this review experiments done in Japan, Europe and in the US for the in-situ large scale destruction of NOx and VOCs are described: extrapolating to $CH_4$ seems reasonable.

Preliminary results with methane presented by Espagnol [48] were quite promising. In 2006, they described the "*Impact of a photocatalytic cover during the storage period of pig slurry on gaseous emissions*". The slurry resulted from the fattening of 54 pigs on slatted floors splitted between two experimental vats of 13 $m^3$ and stored outside for a period of three months. One of the vats was overlaid with a pilot photocatalytic cover. Gaseous emissions of the two vats were continuously measured during 57 days using a tracer method to measure the flows. Results showed an efficiency of the photocatalytic covering with an oxidation of 59% of the emissions of ammonia ($NH_3$) and of 71% of the emissions of $CH_4$ from the slurry.

Very interesting results with $CH_4$ were also published by Guarino and Costa [50,51] and confirm the results from Espagnol [48] although experimental conditions were different. In 2008, they used "*Photocatalytic $TiO_2$ coating to reduce ammonia and greenhouse gases concentration and emission from animal husbandries*". They conducted field experiments aimed at determining effects of coating pig house walls with a $TiO_2$ catalytic paint, and to assess the potential efficiency of this simple painting technique as a low cost diminution of polluting gas emissions. The trial was performed in two identical mechanical ventilated farrowing rooms. Environmental parameters, ventilation rate and gas concentrations were continuously monitored in the two units throughout a 28 days production cycle. Using 36W UV light lamps, average concentration of $CH_4$ was reduced by 15 to 27%.

Using a continuous flow reactor of 1.4 l, Liu [41] obtained 50% methane removal rate at a flow rate 10 $l.min^{-1}$, with a $CH_4$ concentration of 4.5 $mg.m^{-3}.min^{-1}$, using 15W UV lamps. Meanwhile Bellobono [47,49] studied the photo-mineralization of methane in air (10.0-1000 ppm) in an annular laboratory-scale reactor, by photocatalytic membranes immobilising $TiO_2$ with flow rates from 4 $m^3.h^{-1}$ till up to 400 $m^3.h^{-1}$. Bellobono also studied the photo-mineralization of $CH_4$ in water [53].

A more recent work by Shimura and Yoshida [52,53] has been devoted to photocatalytic steam reforming of methane ($CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$) around room temperature over modified (Pt-loaded) and unmodified sodium tantalate or calcium titanate photocatalysts. Photocatalytic water decomposition simultaneously proceeded with photocatalytic steam reforming of methane. Yields were still quite poor, but the main goal of this research was to produce $H_2$ and not the total oxidation of $CH_4$.

Selective photocatalytic conversion of $CH_4$ by partial oxidation or by coupling in order to obtain some useful organic products like $CH_3OH$, syngas, formaldehyde or ethane has been reviewed [54,55]($CH_4 + xO_2 \rightarrow CO_2 + CH_3OH$ or CO or $H_2$ or HCHO, or HCOOH or C2-C6 compounds). Very often partial oxidations of $CH_4$ by selective photocatalysis give $CO_2$ as an important by-product, especially in the case of low yields or low selectivity.

Although these processes (steam reforming or partial oxidation of $CH_4$) are intended to photocatalytically convert concentrated methane to produce liquid or gaseous fuels, these photocatalytic conversions can also help reducing the RF from diluted atmospheric $CH_4$ and should therefore be kept in mind.

### 2.3. Photocatalytic reduction of nitrous oxide

The largest source of nitrous oxide ($N_2O$) is agriculture, driven mainly by the use of synthetic nitrogen fertilisers, but other important sources are fossil fuel combustion, biomass burning, ammonia from livestock manure and from the industrial production of nitric acid and of adipic acid used in nylon manufacture. $N_2O$ is also formed in soils and oceans throughout the world by a natural biogeochemical nitrogen cycle: the microbial processes of nitrification of ammonium and denitrification of nitrate. As they are predominantly biogenic in origin, $N_2O$ emissions are difficult to estimate, but the quantity of this gas has virtually doubled since the beginning of the industrial age. The concentration of $N_2O$ in the atmosphere continues to increase (0.2–0.3% yearly) and this increase appears to be caused mainly by anthropogenic activities.

$N_2O$ is the third most important of the LLGHGs in global warming terms accounting for 6.2% of the total global RF. Although it only comprises 320 parts per billion of the earth's atmosphere, it's contribution to GW is important as it has a $GWP_{100}$ nearly 300 times greater than that of $CO_2$.

In 1974 Winter [56] studied the thermal decomposition of $N_2O$ over 31 metallic oxides, so its thermal catalytic decomposition has been known since a long time. In 1971 Blyholder and Tanaka [57] studied the photocatalytic decomposition of $N_2O$ on zinc oxide but at temperatures in the range of 371 to 431°C, where thermal catalysis was predominant. Kapteijn [58] gave an overview of the ongoing activities in the area of the decomposition of $N_2O$, over solid catalysts, including metals, supported or unsupported pure and mixed oxides, and zeolitic systems.

The photocatalytic reduction of $N_2O$ at room temperature was described later. From 1993 to 1995, Ebitani [59,60,61] described the photodecomposition of $N_2O$ into $N_2$ and $O_2$ on Cu-exchanged ZSM-5 zeolite at 278 K. The dependence of the photocatalytic decomposition rate of $N_2O$ on the wavelength of the irradiated light (<300 nm) revealed the importance of the excitation of monovalent Cu ions. They also described rare earth ions as heterogeneous photocatalysts for the decomposition of $N_2O$. In 1998, Kudo [62] studied the photocatalytic reduction of $N_2O$ on Ag- and Cu-supported $TiO_2$ powder at room temperature in the presence of water and methanol vapour. In 2000 Sano [63,64] studied the photocatalytic decomposition of $N_2O$ into nitrogen $N_2$ on highly dispersed $Ag^+$ ions on $TiO_2$ with $CH_3OH$ as reducing agent. In 2001 Rusu [65] studied the $N_2O$ photoreduction into $N_2$ on $TiO_2$ powder at 157 K with UV irradiation in the range 2.1–5.0 eV.

From 2000 to 2004, in a series of papers Ju, Matsuoka and Anpo [66,67,68,69,70,71] studied the photocatalytic decomposition of $N_2O$ into $N_2$ and $O_2$ on Cu (I) ion catalysts anchored onto various oxides and of silver (I) ion catalysts anchored within zeolite cavities and of several ion-exchanged ZSM-5 catalysts (silver (I), lead (II)). A review from Matsuoka and Anpo [72] reported that transition metal oxides (Ti, V, Mo, Cr) incorporated within the framework of zeolites as well as transition metal ions ($Cu^+$, $Ag^+$, $Pr^{3+}$) exchanged within the zeolite cavities exhibited high and unique photocatalytic activities for various reactions such as the decomposition of $N_2O$ into $N_2$ and $O_2$ or the reduction of $CO_2$ with $H_2O$ to produce $CH_4$ and $CH_3OH$. Recently, Chen and Matsuoka [73] found that the introduction of Mn ions into Cu(I)-ZSM-5 enhanced the photocatalytic activity for the direct decomposition of $N_2O$ into $N_2$ and $O_2$ at 298 K.

Ebitani [74] also described a praseodymium-exchanged zeolite highly active heterogeneous photocatalyst for the stoechiometric decomposition of $N_2O$.

More recently, in 2008 Guarino [50] conducted field experiments aimed at determining effects of coating pig house walls with $TiO_2$ photocatalytic paint in order to assess the potential efficiency of this simple painting technique, and noted a reduction of 4% of $N_2O$ levels. Although this reduction level of $N_2O$ could seem modest, it is worth noting that all previous reported experiments were carried out at the laboratory scale and that this experiment was practiced indoor, with an air ventilation flow rate from 780 to 6690 $m^3.h^{-1}$, 52% relative humidity and with 150 $m^2$ of a 70 $g.m^{-2}$ $TiO_2$ paint. This experiment was designed to reduce $NH_3$ emissions and thus was performed with a low cost unmodified $TiO_2$ photocatalytic paint. The catalyst was not doped with other metals and no methanol was added as reducing agent, so it was not optimal for $N_2O$ reduction.

Indeed, Ag- and Cu- supported $TiO_2$ photocatalysts show higher activity for the reduction of $N_2O$ to $N_2$ at room temperature in the presence of $CH_3OH$ or $H_2O$ vapour.

Nevertheless, as $N_2O$ can be a by-product of $NH_3$ photocatalytic oxidation (PCO), Kolinko [75] investigated the most suitable photocatalysts that minimized $N_2O$ output during $NH_3$ PCO.

United Nations anticipate an increase of world population from 6 billion in year 2000 to 9 billion by 2050 [76], which requires expansion of the land area devoted to crops in order to feed the planet and accommodate the current development of biofuels. Recently, Beaulieu [77,78] made new estimates of stream and river $N_2O$ emissions and found them to be three times greater than estimated by the Intergovernmental Panel on Climate Change.

Measures to limit or reduce agricultural $N_2O$ emissions seem difficult, especially with the increasing global population. The photocatalytic reduction of $N_2O$ might help reducing its concentration in the atmosphere.

Figure 1 from NOAA observations (source IPCC [79]) shows the LLGHGs global trends versus time

***Insert figure 1***

## 2.4. Photocatalytic oxido-reduction of chlorofluorocarbons and other haloalkanes

Halocarbon gas concentrations have increased primarily due to human activities. Principal halocarbons include chlorofluorocarbons (CFCs), which were used as refrigeration agents and in other industrial processes. Even if their concentration in the atmosphere are slowly decreasing, all together they still represent almost 12% of the total radiative forcing of LLGHGs, and among them CFC-11 and CFC-12 account for 8.8%.

Some characteristics of other some minor GHGs are shown in Table 4 [80].

***Insert table 4***

Tanaka [81] studied the photodegradation of HCFC and HFC on several metal oxides. The degradation rate was in the order: $TiO_2$-ZnO > $Fe_2O_3$-kaolin $\geq$ $SiO_2$ $\geq$ $Al_2O_3$. The main degradation products were $CO_2$, $Cl^-$ and $F^-$.

### 2.4.1. CFC-12

Although $TiO_2$ based catalysts have been used for a long time for thermal decomposition of CFCs [82,83], Tennakone and Wijayantha [84] were, in 2005, among the first to report that CFCs could be photocatalytically mineralized with $TiO_2$. They demonstrated that dichlorodifluoromethane (CFC-12, $CF_2Cl_2$) could be readily photo-oxidized by UV radiation at 366 nm in the presence of fine crystallites of $TiO_2$. The products detected were $CO_2$, $Cl^-$ and $F^-$ ions and chlorine ($Cl_2$).

Wylie [85] also observed CFC-12, CFC-11 and HCFC-22 decomposition on oxide surfaces under ultraviolet-visible photolysis (at $\lambda > 300$ nm) and/or thermal treatment.

It is worth reminding that CFC-12 has a very high $GWP_{100}$ of 10900 and with a radiative forcing of 0.169 it represents 6.2% of the total of the LLGHGs and ranks 4th in importance.

### 2.4.2. CFC-11

Kutsuna [86] studied the adsorption and reaction of trichlorofluoromethane (CFC-11, $CCl_3F$) on various particles and confirmed the surface induced degradation of $CCl_3F$ in air under photoirradiation at room temperature with UV wavelengths above 310 nm on some metal oxides. Calhoun [87] described the CFC-11 dehalogenation through a reductive chain reaction upon illumination of aqueous, air-free suspensions of $TiO_2$ particles in the presence of formate ions. Winkelmann [88] proved that CFC-11 could be photoreduced in aqueous suspensions of $TiO_2$ particles containing $HCO_2^-$ ions and air.

CFC-11 has a $GWP_{100}$ of 4800 and with a radiative forcing of 0.061 (2.2% of total) and ranks 5th in importance among LLGHGs.

### 2.4.3. HCFC-22

Wataru [45] studied the photocatalytic decomposition of halocarbons by using $TiO_2$ and the decomposition rate was found to be the highest for chlorodifluoromethane (HCFC-22).

HCFC-22 has a RF of 0.033 (1.2% of total) and ranks 6th in importance among LLGHGs.

### 2.4.4. CFC-113

Weaver [89] showed that reductive dehalogenation of trichlorotrifluoroethane (CFC-113), took place upon illumination of air-free suspensions of $TiO_2$ particles containing formate ions.

CFC-113 has a RF of 0.024 (0.9% of total) and ranks 7th in importance among LLGHGs.

### 2.4.5. Other halogenated derivatives

The photocatalytic degradation of several other CFCs has been reported in the literature. For instance, Sangchakr [90] studied the photodegradation of $CH_3CF_2H$ (HFC-152a) at 185 nm and 254 nm with $TiO_2$. Although degradation rate was nearly twice as large at 185 nm as at 254 nm, almost complete mineralisation was only obtained with $TiO_2$ at 254 nm.

Delprat [91], studied the aqueous degradation over $TiO_2$ photocatalyst of CFC-11 as well as $CH_3$-$CCl_2F$ (HCFC-141b) and $CF_3$-$CH_2F$ (HFC-134a) under UV light. The Japanese agency of industrial science and technology deposited a patent [92] on a new catalyst for the removal of chlorofluoromethanes. Decomposition of chlorofluoromethanes was achieved by irradiation at a wavelength lower than 400 nm over $TiO_2$ photocatalyst doped with Pd, Rh, Ir, or Ru.

Other classes of GHGs are included in the Montreal Protocol for Substances that deplete the ozone layer like halons and halogenated solvents containing chlorine and bromine: methyl chloroform ($CH_3CCl_3$) [93], carbon tetrachloride ($CCl_4$) [94,95], bromochloromethane ($CH_2BrCl$) [96], etc. These chemicals can also be eliminated by photocatalytical oxido-reductions. For instance the phototransformation of bromochloromethane and other halons and halomethanes containing bromine and fluorine ($CBr_3F$) or chlorine and bromine ($CBrCl_3$, $CHBrCl_2$, $CH_2BrCl$) have been investigated by Calza under aerobic and anaerobic conditions over $TiO_2$ photocatalyst both in homogeneous and heterogeneous systems [96]. Both oxidative steps and reductive steps were detected during the degradation pathways. Several halogenated intermediates and oxygenated compounds were identified. Alberici [97] also described photocatalytic degradation of chlorinated volatile organic compounds.

In aqueous media neutralisation of halo acids might be necessary. In the gaseous phase, deactivation of the photocatalysts may occur by $F^-$ or $Cl^-$ contamination [98], but as for $NO_3^{2-}$ or $SO_4^{2-}$ deactivation of catalysts during the photocatalytic oxidation of NOx or sulphur containing compounds, respectively, the reactivation or regeneration of the photocatalysts might be easy and rapid by rinsing them with water [99,100,101], to remove the corresponding acids.

Concentrations in the atmosphere of CFCs and of many other GHGs are within the ppb ($10^{-9}$) range. Studies on the photocatalytic oxidation of air pollutants have primarily dealt with concentration range from low-ppm to high-ppm levels, typically 10-1000ppm. Jo [102] evaluated the technical feasibility of applying $TiO_2$ photocatalytic technology to cleansing low-ppb concentrations of VOCs and found that their destructions were up to nearly 100%.

## 3. PART 2: The potential of photocatalysis against other agents causing climate change

In this second part of the review, current progress in the area of photocatalysis of other agents causing climate change is discussed, in particular direct photocatalytic reduction of $O_3$; photocatalytic oxidation of NOx, soot and $O_3$ precursors over some semi-conductor photocatalysts, in particular over $TiO_2$ based catalysts.

### 3.1. Other global warming contributors

Figure 2 (from IPCC 2007 AG4) shows that the greenhouse forcing of methane, halocarbons, tropospheric ozone, $N_2O$ and black carbon BC (soot), compare in magnitude to the radiative forcing by $CO_2$.

***Insert figure 2***

For Hansen and Sato [103] (figure 3) direct and indirect forcing by $CH_4$ (0.7 $W/m^2$) is half as large as that of $CO_2$ and the total forcing by non-$CO_2$ GHGs (1.4 $W/m^2$) equals that of $CO_2$.

***Insert figure 3***

### 3.2. Tropospheric Ozone

Tropospheric ozone ($O_3$) is, after $CO_2$ and $CH_4$, the 3rd most important contributor to greenhouse RF. $O_3$ is not an LLGHGs. Its concentrations are highly variable in space and time, the highest concentrations being observed under certain weather conditions over industrial regions.

Tropospheric ozone, which is produced by man-made emissions of $O_3$-forming gases, has increased of 35% from 1750 to 2000, and adds $0.35 \pm 0.15$ W $m^{-2}$ according to the IPCC 3rd assessment report [104] or $0.5\pm 0.2$ W $m^{-2}$ according to Hansen estimates (figure 3).

Ozone is produced in the troposphere by photochemical oxidation of CO, $CH_4$ and non-methane volatile organic compounds (NMVOCs) in the presence of NOx. For some authors, depletion of hydroxyl radicals may be one of the indirect causes of increasing atmospheric methane and thus of tropospheric $O_3$.

Methane is the dominant VOC precursor to global tropospheric $O_3$ and, as such, has significant implications on ozone level. Thus, its photocatalytic removal from the atmosphere can reduce $O_3$ levels. According to Fiore [105], with a 3-D model of tropospheric chemistry, reducing anthropogenic $CH_4$ emissions by 50% nearly halves the incidence of U.S. high-$O_3$ events and lowers global RF by 0.37 W.$m^{-2}$ (0.30 W.$m^{-2}$ from $CH_4$, 0.07 W.$m^{-2}$ from $O_3$).

### 3.2.1. Direct photocatalytic destruction of tropospheric Ozone

Gas phase $O_3$ decomposition by thermal catalysis has been reviewed by Dhandapani [106]. Ground level ozone is a GHG and is associated with adverse health and welfare effects.

On one side, direct photocatalytic removal or destruction of tropospheric $O_3$ is possible at room temperature, for instance over $TiO_2$ photocatalysts [107,108],silver or silver oxide loaded $TiO_2$ [109], or Pt-loaded $TiO_2$ [110].

On the other side, a recent study [111] revealed for the first time the production of $O_3$ from $TiO_2$ coated glass surfaces with nitrate anions (either premixed with $TiO_2$ as $KNO_3$ or deposited from gaseous NOx) irradiated with broad-band light. As stratospheric ozone forms a protective layer that shields life on Earth from the Sun's harmful rays, international regulations work at protecting this "good" ozone in the upper atmosphere through regulations on ozone depleting substances like CFCs. This discovery might help fighting against the hole in the ozone layer by some kind of high altitude photocatalytic techniques yet to be developed.

### 3.2.2. Indirect photocatalytic elimination of tropospheric Ozone by photocatalytic mineralization of VOCs, CO and NOx

As NOx, CO, and VOCs are $O_3$ precursors, and as these local pollutants can be reduced by photocatalytic processes an indirect way to reduce tropospheric ozone is through the photocatalysis of NOx, CO and VOCs.

Photocatalytic oxidation (PCO) reactors are able to eliminate many VOCs. Hodgson [112] reported an experimental evaluation of a PCO device with UV light and a tungsten oxide ($WO_3$) modified with $TiO_2$ photocatalyst. The device was challenged with complex mixtures containing 27 VOCs usually present in office buildings and proved to be quite efficient.

Several authors described the PCO of CO [113,114,115,116]. Already in 1972, Formenti [28] observed that oxygen at 25°C was adsorbed on some oxides ($Al_2O_3$, $Fe_2O_3$, $GeO_2$, $SiO_2$, $TiO_2$, $V_2O_5$, $ZrO_2$), in particular on $TiO_2$, and that in the presence of UV radiation, as a labile species, $O_2^-$ reacted under irradiation with paraffins, olefins, CO, $SO_2$, and NO, to give products of partial or of total oxidation.

Since then, the level of activity in this field increased exponentially and a huge amount of research has been conducted as illustrated by the very high number of related publications.In 1994 Blake [117] in his first report entitled: "*Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air*", included 663 references collected since the middle of 1993. Blake's first update till 1995 contained 574 additional references. The 1997 update contained 518 new citations and the 1999 update contained 1,517 new references. In 2001 Blake [118] reviewed 1555 new articles.

### 3.3. Particulate matter

NOx pollution is often associated with particulate matter (PM), which gives important concern about its effects on human health. Average ranges of particulate matter concentrations and chemical composition show significant spatial and temporal variations in airborne.

Vione [119] in a tutorial review explained the tropospheric photochemical reactions on particulate matter.

In their large scale experiments in weaning rooms of a swine farm containing 391 pigs, Costa and Guarino [51] obtained significantly lower levels of $PM_{10}$ in the treated room by a $TiO_2$ photocatalytic paint (48 µg vs 58 µg).

In this review PM elimination or destruction by photocatalysis is not addressed, but it is worth noting that several articles described the photocatalytic elimination, in air and/or in water, of polycyclic aromatic hydrocarbons (PAHs) [120], dioxins [121], ammonia [122,123], sulphate [124,125], sulphur compounds [126,127], formaldehyde [128,129], bacteria, spores and viruses [130,131,132] and even biomass [133,134]. All these products are among the constituents of PM, with carbon, mineral dust, pollen, nitrates, … To reduce secondary fine PM effectively, beside the emissions of NOx and SOx, the ammonia emissions need to be decreased and this could also be done by photocatalysis.

The 2010-2013 European Commission Life PhotoPaq project [135] (*Demonstration of Photocatalytic Remediation Processes on Air Quality*) addresses the reduction of pollutants such as nitrogen dioxide, hydrocarbons and particulates. In two different European cities a tunnel and a road have been treated with a photocatalytic additive. Seven research groups from France, Belgium, Greece and Germany, as well as an Italian-French industrial corporation, are taking part in the project. The first field test in a road tunnel in Brussels is scheduled for 2011.

### 3.4. Soot and Black Carbon

Soot and Black Carbon (BC) warm the Earth by absorbing heat in the atmosphere and, when deposited on snow and ice, by reducing albedo, the ability to reflect sunlight. Black carbon deposition on snow is a major source for arctic sea ice retreat and melting glaciers. BC aerosol albedo, causes a semi-direct reduction of cloud cover, and reduces cloud particle albedo. All these effects cause global warming.

BC is formed through the incomplete combustion of fossil fuels, biofuel and biomass, and is emitted in both anthropogenic and naturally occurring soot. Soot is a general term that refers to impure carbon particles resulting from the incomplete combustion of a hydrocarbon. The main constituents of soot are PAHs, many organic acids and BC (light absorbing elemental and organic carbon particles). Atmospheric brown clouds [136] (ABCs) are regional scale plumes of air pollution that consist of copious amounts of tiny particles of soot (containing BC), sulphates, nitrates, fly ash and many other pollutants.

In its 2007 report, the IPCC [137] estimated for the first time the direct RF of BC from fossil fuel emissions at + 0.2 W/m$^2$, and the RF of BC through its effect on the surface albedo of snow and ice at an additional + 0.1 W/m$^2$. But many of the scientists mentioned in the IPCC report estimate , in more recent studies that emissions from BC are the second largest contributor to global warming after carbon dioxide emissions. Hansen [138,139] estimated the climate forcing of BC at 1.0±0.5 W.m$^{-2}$. For Ramanathan and Carmichael [140,141] the BC forcing of 0.9 W.m$^{-2}$ (with a range of 0.4 to 1.2 W.m$^{-2}$) is as much as 55% of the $CO_2$ forcing and is larger than the forcing due to all the other GHGs together. A relatively cheap, fastand simple way to significantly rein in global warming, especially in the short term, consists in decreasing black carbon emissions. Conceivably a reduction of climate forcing by 0.5 W.m$^{-2}$ or more could be obtained by reducing black carbon emissions from diesel fuel and coal.

### 3.4.1. Photocatalytic oxidation of soot

Many authors like Hansen [139] or Jacobson [142] often talk indifferently of soot or BC. IPCC 2007 wrote [143]: "*Fossil fuel and biomass burning have increased aerosols containing sulphur compounds, organic compounds and black carbon (soot)*". Although there are slight differences between black carbon and soot, we assume that their oxidation process and their photocatalytic mineralization are similar. In this chapter photocatalytic abatement of soot is reviewed.

Recently D'Auria [144] compared the photochemical degradation of crude oil by direct irradiation, photocatalysis, and photocatalysis on zeolite. They found that photocatalysis gave extensive degradation of crude oil: linear alkanes were degraded for 98.66%, branched alkanes were reduced for 97.31%, cyclic alkanes for 96.04%, while aromatic compounds and alkenes were reduced for 99.54 and 98.38%, respectively. Some of these compounds might be considered as VOCs, some others as soot. It was not until 2002 that Lee [145] monitored the solid-phase photocatalytic degradation reaction of black carbon soot deposited on a $TiO_2$ film by weight loss measurement. They also investigated the role of migrating OH radicals during the solid phase photocatalytic reaction at the soot/$TiO_2$ interface. The presence of $O_2$ was essential in the photocatalytic soot oxidation. Adding water vapour efficiently enhanced the photooxidation rate of soot as a precursor of OH radicals, the main oxidant species, meanwhile introducing 2-propanol reduced the photooxidation rate of soot as an OH radical scavenger. In 2004 during experiments of direct, lateral and remote photocatalytic destruction of soot by titania, Lee [146] found evidence for the photo-generation of an oxidising species which was both surface mobile and capable of air-borne diffusion.

In 2006 Mills [147] described the photomineralisation of soot by P25 titania films which exclusively involved the oxidation of carbon to $CO_2$.

Then, Chin [148,149,150] developed a kinetic model for direct photocatalytic soot oxidation by thin films of $TiO_2$, and in 2009 they published an article [151] about quantitative photocatalysed soot oxidation on $TiO_2$.

Many scientists mentioned in the 2007 IPCC report, estimated that reducing BC and soot emissions could be the fastest strategy for slowing climate change [152]. Black carbon alone is estimated to have a $GWP_{100}$ of 1,055 to 2,240. Fossil fuel soot has a lower estimated $GWP_{100}$ of 840 to 1,280, as a result of mixing with cooling aerosols and particulate matter.

Soot and BC stay from several days to weeks in the atmosphere, whereas $CO_2$ has an atmospheric lifetime of more than 100 years. Given black carbon's relatively short lifespan, according to Jacobson [153], reducing black carbon emissions is very likely to be the fastest method of slowing global warming in the immediate future. Photocatalytic BC and soot oxidation processes may contribute to this goal.

### 3.5. Photolysis of $SF_6$ and $SF_5CF_3$

The global warming attributable to sulphur hexafluoride ($SF_6$) and trifluoromethyl sulphur pentafluoride ($SF_5CF_3$) is currently low (0.003 $W.m^{-2}$), but on a per molecule basis they might be among the most potent GHGs.

$SF_6$ is a gas with a warming potential $GWP_{100}$=23900 and a lifetime of 3200 years and has as a very strong radiative forcing [154] of 0.52 $W.m^{-2}.ppbv^{-1}$ meanwhile the radiative forcing of $SF_5CF_3$ is estimated to 0.59 $W.m^{-2}.ppbv^{-1}$. Due to their progressive accumulation in the atmosphere, they are believed to aggravate the Earth's greenhouse effect in the long run since once emitted into the atmosphere, their chemical inertness explains their long lifetimes as they are removed exceedingly slowly.

Several thermal catalysts [155] have been found efficient to decompose $SF_6$: $AlPO_4$, $CePO_4$, $YPO_4$, and $Zr_3(PO_4)_4$ at 800-1000 K. Dervos [156] observed that in the presence of moisture on a few micrometers-thick $Al_2O_3$ film, hot $SF_6$ molecules form a diffused over layer of $AlF_3$, the by-products in the gas matrix being mainly sulphur oxides at temperatures below 300°C. The application of photochemical techniques to eliminate $SF_6$ and $SF_5CF_3$ is a relatively new field. With the purpose of developing novel remediation techniques for $SF_5X$ pollution ($X = F$ or $CF_3$), Huang published a series of papers on their efficient abatement under UV irradiation at 185nm in the presence of acetone [157], propene [158] or styrene [159]. To decompose more than 90% of the initial $SF_5X$, 360 min of irradiation were necessary in the presence of styrene or propene, but only 100 min in the presence of acetone. It is noteworthy that the whole system has not yet been totally optimized. As-fluorinated intermediates and products were expected, the photodegradation studies were conducted in a homemade stainless steel reaction cell, and no photocatalyst was used. But if photolysis is possible, the photocatalysed reaction would probably also be obtained. More research, time and effort for the application of the photocatalytis in this field are needed. Recently, Song [160] reported the photodegradation of $SF_6$ by reductive radicals generated by UV light on polyisoprene surface from natural rubber.

### 3.6. What about $NF_3$?

Although not yet well documented and not yet included in the Kyoto list of GHGs, nitrogen trifuoride ($NF_3$) has a potential greenhouse impact [161] larger than that of the industrialized nations' emissions of PFCs or $SF_6$, as $NF_3$ has a lifetime of 550 years, a $GWP_{100}$ of 17200 and its production in 2008 was equivalent to 67 million metric tons of $CO_2$. No publication was found on photocatalytic abatement of $NF_3$, but Vileno [162,163] investigated the thermal decomposition of $NF_3$ by various oxides and also by Ti, Si, and Sn powders. Using Na-doped alumina, conversion of $NF_3$ dropped off faster than conversion with the undoped alumina. In all cases, NOx and the corresponding metal fluorides were the only major products from the reactions. The thermal decomposition of $NF_3$ using alumina can occur at temperatures as low as 100°C. Therefore eliminating $NF_3$ seems easier than $SF_6$ or $CF_4$, and thus photocatalytic decomposition should therefore be possible.

## 4. PART 3: large scale indoor and outdoor applications of photocatalysis to cleaning off atmospheric environment and future development perspectives

In parts 1 and 2, the potential of photocatalysis at the laboratory scale to transform LLGHGs and SLCFs has been reviewed. Here, examples of real word applications are provided and future perspectives envisioned.

Many authors reviewed the literature about the destruction of VOCs, CO and NOx by photocatalytic oxidation at the laboratory scale, but also in indoor air: some of these reviews and articles are summarised in Table 5.

In the past few years, Japan, US, Europe and Hong Kong [187,185] have tested photocatalytic oxidation PCO technology in community-scale environmental remediation. Under light illumination NOx will be oxidized to nitric acid, neutralized by the alkaline materials in concrete, and washed away by rain.

***Insert table 5***

A Patents' overview of the application of $TiO_2$ photocatalysis for air treatment has recently been done by Paz [188].

In Japan, Ibusuki [189] conducted tests in a roadside of a 6 lane bound highway in Tokyo with an average traffic of 113,000 vehicles a day. The average removal percentage for NOx with windowed panels was 31-69% during the field tests. VOCs and $SO_2$ were respectively removed by 17-20% and by 67-78%. For NOx, the estimated rate was 3 $mmol.m^{-2}.d^{-1}$. The capacity of the photocatalytic sheet for NOx removal was 20 $mmol.m^{-2}$. Mo [172] reported that $TiO_2$ has been applied in coatings in many Japanese cities, such as Osaka, Chiba, Chigasaki, Suitama and Shinatoshin. At least 50,000 $m^2$ of surface area in Japan has been covered with such coating, and the authors claimed that the daily removal rate goes from 0.5 to 1.5 $mmol.m^{-2}$ and that the photocatalytic material could maintain its effectiveness with very little performance deterioration. Also, in 1999, a $TiO_2$ coating was used to coat highway sound barriers in Osaka, Japan, the purpose of which was to reduce NOx pollutants as well as providing a self-cleaning effect. According to several of the authors cited, the tested photocatalytic coatings have a potential to economically reduce emitted NOx, CO and VOCs at ambient conditions and are nearly maintenance-free. These large scale in-situ de-polluting systems were tested in order to evaluate the costs/benefits of photocatalytic coating on walls, pavements, sound barriers and other road structures for the on-site destruction of NOx, and to develop advanced, cost-effective catalytic coatings on concrete, asphalt and other road surfaces.

In tests carried out in Houston [190], the preliminary estimates of NOx removal for Harris County were very promising: NO removal of around 0.01 $g.m^{-2}$ over a 12 hour daytime period assuming an effective concentration of 2000 ppb near the catalytic surfaces. The NO concentration coming out of vehicles in the vicinity was 650 ppm, meanwhile at ambient conditions NO concentration was around 200 ppb. This represented a 28% removal or, assuming that pavements last for 5 years, 50,000 ton.yr$^{-1}$ at a cost of $200 per ton. The authors concluded that the reduction on the number of high ozone days could be significant to allow sustainable economic developments in major Texas urban areas (e.g., Houston-Galveston-Brazoria and Dallas-Ft. Worth). PICADA [191] was a research group partially funded by the European Union and comprised universities and companies from England, France, Italy, Denmark and Greece. They have produced numerous photocatalytic active materials. In particular, TxActive, produced by Italcementi, is a photocatalytic cement that has entered the commercial market. Some of their results have been published [192]. In the frame of the PICADA project (2002-2005) several laboratory scale tests, macro scale tests and tests on pilot sites were conducted [193,194,195]. The laboratory tests showed 80% reduction in levels of NOx (especially NO) near $TiO_2$ containing paints and cements, meanwhile in canyon street tests, NOx concentrations were reduced by 40-80% depending on the differences in emission sources, wind direction and orientation of the walls. In Germany, nitrogen oxide-reducing paving slabs developed by F. C. Nüdling Betonelemente are currently being tested in the cities of Erfurt and Fulda. Proof of the effectiveness of these paving slabs has subsequently been provided by the Fraunhofer Institute. The work was funded by the German Environment Foundation. Measurements equally taken at a height of three meters above the Gothaer Platz in Erfurt, which is already paved with “Air Clean” paving slabs, revealed an average degradation rate of 20% for $NO_2$ and 38% for NO. Measurements recorded from 14 to 23 months after they were laid revealed no change from the initial degradation capability of the photocatalyst: they remain stable over the long term. The Baroque city of Fulda is currently embarking on this new way to fight air pollution: the paving slabs are to be laid the length of Petersberger Straße. In Belgium a pilot project of 10 000 m² was constructed in Antwerp [196]. Measurements to reveal the air purifying efficiency in situ and the durability of this efficiency were programmed. The final results of the 4-year project obtained in laboratory as well as on site at the Leien of Antwerp indicated a durable efficiency towards NOx levels reduction, which was in favour for the diminishing of the risk on ozone formation.

All these results obtained on street-air purification show that a successful decomposition of NOx and VOCs along concrete paving stone surfaces is feasible by using PCO in the presence of UV light. Ozone can also be decomposed to oxygen over photocatalysts according to the literature (vide supra). New experiments should not only concentrate on reduction levels of NOx, CO and VOCs, but also on other GHGs like $CH_4$ or $N_2O$.

### 4.1. Photocatalytic activity of $TiO_2$

Titania is known as a semiconductor material which exhibits photocatalytic activity for decomposition of many organic substances under UV light irradiation [197].

Up to now, $TiO_2$ has undoubtedly been proven to be the most excellent photocatalyst for the decomposition of many organics under UV irradiation [198].

When exposed to solar radiation it acts as a catalyst for the photodecomposition of pollutant molecules adsorbed on its surface and the transformation into non-toxic or less toxic compounds. With nanomaterials, $TiO_2$ photocatalysed oxidation or reduction of many pollutants has become a reality in every day's life. Incorporation of $TiO_2$ in building materials, glass or surface coatings [199] imparts self-cleaning and de-polluting properties to them. $TiO_2$ photocatalysis has been studied in large scale and open air to reduce NOx and VOCs pollution [200] in several countries (vide supra).

Since the early twentieth century, $TiO_2$ has been widely used in sunscreens, lipsticks, ointments, toothpaste, paints, and as a pigment. Regarding its commercial availability, suitable optical and electronic qualities, chemical stability and non-toxicity, $TiO_2$ seems to be the most convenient candidate for photocatalytic conversion of many mineral and organic compounds and especially for GHGs and other climate forcers. Therefore, this paper focused mainly on the photocatalytic conversion of GHG on the $TiO_2$-based catalysts [201], but also other photocatalysts have been cited [202].

### 4.2. Visible light $TiO_2$ photocatalysts

The major components and impurities of the earth's atmosphere ($N_2$, $O_2$, $H_2O$, GHGs like $CO_2$ $CH_4$, CFCs, etc.) are almost totally transparent to solar radiation. Only a small portion of the energy of solar light is found in the wavelength $\lambda \leq 200$ nm spectral region where electronically excited states of these molecules can be formed. In other words, most of the energy of the solar flux cannot participate in such direct photochemical reactions [203]. Photocatalysis with visible-light photocatalysts can facilitate the photooxidative degradation of organic pollutants [204]

Due to the relatively broad band gap energy of about 3.2 eV, the light absorption of anastase $TiO_2$ takes place in the UV range allowing the absorption of only 4-5 % of solar energy, and resulting in low quanta efficiencies. For this reason, much research is actually focused [205] on broadening the spectrum range, in which $TiO_2$ is capable to absorb visible light, as there is almost 10 times more energy produced by sunlight in the visible than in the UV range.

Strategies to induce visible light activity have been reviewed by many authors and abundant literature exists on the subject [206,207,208,209,210,211] that enumerates the various ways by which modified $TiO_2$ or other semiconductors are effective for the degradation of organic or mineral pollutants using the visible range of the solar spectrum. Among other catalysts, carbon doped, nitrogen-doped and Sn-doped titania photocatalysts show enhanced daylight activity, but also $TiO_2$ doped with rare metals and rare-earth metals. Other strategies to induce visible light activity have been described, like the accumulation of defects on $TiO_2$ nanomaterials.

### 4.3. Recent developments in photocatalysis

Qin [212] reported the novel photocatalytic activity of Yb(3+),Tm(3+)/TiO(2) core/shell nanoparticles under near-infrared (NIR) irradiation. Kogo [213] proved that an Au25-modified $TiO_2$ worked as a photocatalyst both under visible and NIR light (≤860 nm).

These studies demonstrate that NIR energy can be used as the driving source for photocatalysis besides UV and visible light.

Recently, Horikori [214] reported microwave specific effects on photo-assisted reactions. In the case of ZnO, the photoactivity was enhanced by microwaves' magnetic field (non-caloric specific effect), but decreased by the thermal factor originating from the microwaves' electric field. For the same reaction, on the contrary to ZnO, the photoactivity of $TiO_2$ was enhanced by the synergistic effect of both magnetic and electric fields of microwave radiation.

The combination of photocatalysis with other chemical or physical operations might improve the photoprocess performance by synergistic effect [215].

### 4.4. Key research needs

Worldwide, coal mine methane emissions make up approximately 8% of the world's anthropogenic $CH_4$ emissions and approximately 70% of all coal mining related emissions [216] are from underground ventilation air: could photocatalysis be helpful in reducing coal mine $CH_4$ emissions?

In recent years continued breakthroughs have been made in the preparation, modification, and environmental applications of photocatalysis [217]. Photocatalytic reduction of atmospheric levels of almost all GHGs and of air pollution using $TiO_2$ nano-particles and free solar energy at room temperature is a very attracting concept. The processes are almost mature and technically feasible. However, accomplishing this goal in an efficient and cost-effective way will be challenging due to the large volumes of air that must be processed.

Pichat [171] noted that most often, in many laboratory studies, the tests of $TiO_2$ powders. $TiO_2$-containing coatings or photocatalytic reactors are done with only one pollutant at the ppm level. Indoor air contains many pollutants at much lower concentrations, at ppb scale, but with % levels of humidity. Therefore, the interactions to be considered are not those between "dry" $TiO_2$ and ppm levels of pollutants, but competition between $TiO_2$ covered by layers of water and pollutants at the ppbv scale. A mixture of several pollutants from a variety of chemical families at ppbv scale must be investigated, and why not, chosen among GHG and GW contributors.

Photocatalytic reactors can be modular and operate with negligible pressure drop. They have already been scaled up to suit a wide variety of indoor and outdoor air quality and environmental applications [218,219]. But even if photocatalysis already offers good prospects, more research has to be performed before reaching useful giant photocatalytic reactors [220,221] able to filter or purify several $km^3$ of air every day.

Intensified research efforts in this direction are necessary to:

- develop more efficient photocatalysts with enhanced photocatalytic activity and increased specificity, maybe by composite photocatalysts made of semiconductor oxides and high surface area adsorbents [222], or by molecular imprinting [223] in order to induce selectivity among the pollutants to be mineralized;
- choose the best photocatalyst among the numerous candidates, which apart from cost also depend on which pollutants and chemical reactions are considered;
- optimize the different reduction or oxidation processes, mass transport, adsorption of contaminants, contact time, humidity effects, adhesion of photocatalyst to substrates, photocatalyst reactivation in case of deactivation;
- determine how to best deploy and use photocatalytic oxidation or reduction technology;
- ensure that there are no emissions of toxic by-products and no unintended environmental consequences from the large scale use of these catalysts and processes.

This review will maybe promote further R&D efforts in the area of GHGs removal by photocatalysis, for instance to reduce GHGs emissions against coal mining methane, or methane biogas from mechanical and biological fermenting waste composting and treatment. For instance sludge from water treatment plants is often composted or dried inside large greenhouses of up to 5000 $m^2$, without recovery or valorisation of methane biogas: photocatalysis of the exhaust gases should be attempted.

Each square meter of high-performance photocatalytic material, exposed to outdoor sunlight, can remove VOCs and NOx from respectively about 60 and 200 $m^3$ of air per day [224].

The Heat Island Group of the Environmental Energy Technologies Division of the Lawrence Berkeley National Laboratory has investigated novel infrared-reflecting cool roofing materials and examined the feasibility of novel roofing and other construction materials that may clean the ambient air. As many $TiO_2$-based coatings have high solar reflectance and can help keep the building roofs and walls cool, they can reduce electricity use for summertime air-conditioning. Although there is a wintertime heating penalty, Akbari [225] and Konopacki [226] documented net annual energy savings of 10 to 20%. Parker [227] also noted a 12 to 40% kWh peak period demand reduction. According to Rosenfeld [228] a 10% reduction in annual cooling energy use could save each year about $50 per household, which represents about $50 million annual savings for California alone. Cheap $TiO_2$ white paints can help reaching this goal and, maybe, at the same time, destroy harmful pollutants and GHGs.

Increasing the albedo of urban surfaces has received attention as mitigation strategy against urban heat islands. For instance, recently Oleson [229] studied with a global climate model the effects of white roofs on urban temperature and found that urban daily maximum temperature can be decreased by 0.6°C and daily minimum temperature by 0.3°C with annual mean heat-island decrease of 33%. Akbari [230] estimated that with fully implemented white roofs, white pavements and shade trees, the cooling energy savings in U.S. could be of about $100 per air-conditioned house representing about $5 billion per year. Akbari [231] also estimated that about 20% of the national cooling demand could be avoided through a large-scale implementation of heat-island mitigation measures. This amounts to 40 TWh/year savings in cooling-electricity alone.

Already self cleaning glass and paints are identified as elements of a green architecture for destruction of the urban air pollutants. As $TiO_2$ is perfectly compatible with silicate body mixes, the possibility to obtain photocatalytic construction materials, to be used for outdoor applications, such as wall paints, glass, roofs and floor tiles could represent an opportunity to address several of the problems connected with the increasing environmental pollution and global warming problems such as reducing urban heat-island, smog, local pollutants levels as well as GHGs, and at the same time saving energy and reducing $CO_2$ emissions. This can help to mitigate GHG emissions and also provide environmental protection, public health and sustainable development co-benefits.

## 5. CONCLUSION

Many thermal catalytic methods exist for the abatement of $CH_4$, $N_2O$, CFCs, $SF_6$, etc. But the decompositions often take place at high temperatures and the catalysts include expensive rare metals. As the sources of GHGs are numerous and often diffuse, only part of these emissions can be effectively controlled by this type of cleanup methods.

This comprehensive review on photocatalysis techniques at room temperature aims at demonstrating their potential in helping solving the environmental and global warming challenges humanity is currently facing, by demonstrating that photocatalytic technologies could be useful in:

- transforming or converting $CO_2$ gas, back to fuels using solar energy;
- destructing anthropogenic non-$CO_2$ GHG (mainly $N_2O$, $CH_4$, CFCs, etc.);
- eliminating BC and soot (probably also PM), probably the second-largest contributor to global excess radiative forcing after $CO_2$;
- reducing tropospheric $O_3$ and its precursors (NOx, VOCs, $CH_4$, CO).

Photocatalysis looks like a panacea to fight all potent greenhouse gases, as photocatalysed reactions are able to transform or destroy almost all well-mixed, long-lived greenhouse gases - $CO_2$, $CH_4$, $N_2O$, CFC-12 and CFC-11 - which account for about 96% of the direct radiative forcing, and also short-lived climate forcers like VOCs, NOx, BC and soot that have an important contribution to climate change.

The effects of essential parameters on process performance, including light wavelength and intensity, type of reducing agent or oxidant, metal-modified surface, temperature and pressure can be found in the literature cited herein.

However, for successful application of photocatalytic laboratory scale techniques to large scale photodegradation of atmospheric pollutants more research and engineering design need to be performed.

This literature review showed that cheaper photocatalytic technologies for the abatement of GHGs, BC, tropospheric $O_3$ and low-level local pollutants (VOCs and

NOx) can indeed be an effective alternative to limit their increasing tropospheric concentration and thus reduce their contribution to global warming.

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## Captions

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***Figure 1:*** *Global trends of the mixing ratios of well-mixed long-lived greenhouse gases versus time from NOAA observations (IPCC)*

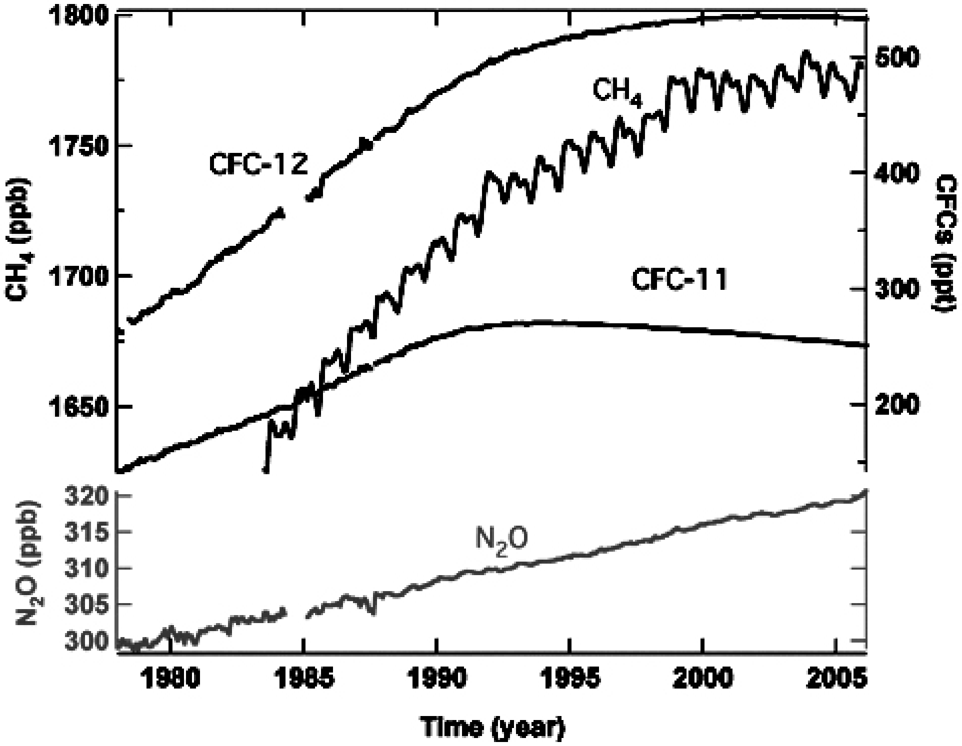

***Figure 2**: Summary of the principal components of the radiative forcing of climate change (IPCC)*

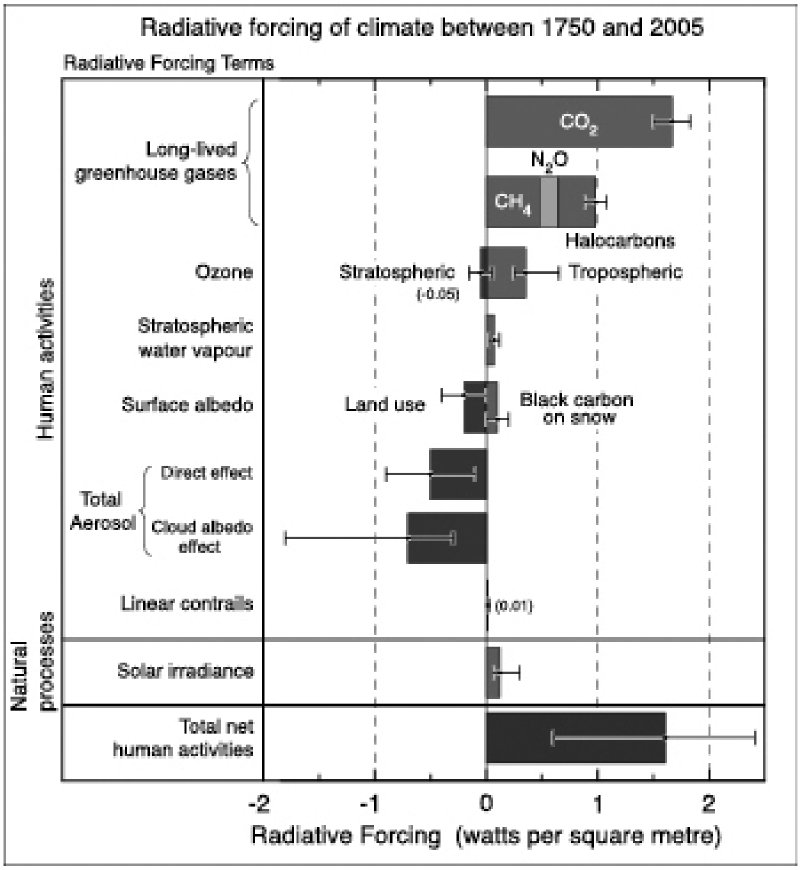

***Figure 3**: Estimated climate forcing between 1850 and 2000 (Hansen 2001)*

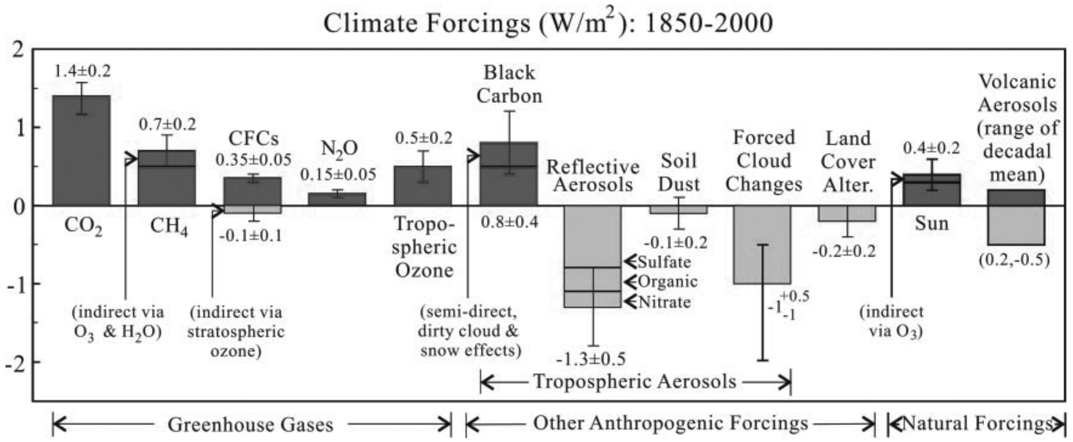

***Table 1:*** *principal GHGs and their characteristics*

| **LLGHG** | **Global Radiative Forcing in 2008 ($W.m^{-2}$)** | **Relative importance** | **$GWP_{100}$** | **Atmospheric lifetime (years)** |
|---|---|---|---|---|
| $CO_2$ | 1.739 | 63.5 % | 1 | More than 100 |
| $CH_4$ | 0.500 | 18.2 % | 25 | 12 |
| $N_2O$ | 0.171 | 6.2 % | 298 | 114 |
| CFC-12<br>Dichloro difluoromethane | 0.169 | 6.2 % | 10900 | 100 |
| CFC-11<br>Trichloro fluoromethane | 0.061 | 2.2 % | 4800 | 55 |
| *15 other minor GHGs* | *0.100* | *3.7 %* | - | - |
| *Total* | *2.740* | *100 %* | -- | -- |

***Table 2**: list of some photocatalysts for $CO_2$ reduction cited in review articles*

| $CO_2$ reduction photocatalysts | Title of the review | Reference |
|---|---|---|
| Ti-MCM-41, Ti-MCM-48, Ti-zeolite, $TiO_2$ zeolite, $ZrO_2$, $Pd/TiO_2$, Re-complex/$TiO_2$, $Pt/K_2Ti_6O_{13}/Fe$, MgO, $Pd/RuO_2/TiO_2$, CuO/ZnO, $LiO_2/TiO_2$, $TiO_2$/Pd/Al2$O_3$, $TiO_2/Pd/SiO_2$,<br>CdS-surface modified by Thiol-$TiO_2$, CdS-surface modified by DMF-$ZrO_2$ | Photocatalytic Process for $CO_2$ Emission Reduction from Industrial Flue Gas Streams | Usubharatana [12] |
| GaP, GaAs, ZnS, $SrTiO_3$, $Cu/TiO_2$, $TiO_2$/zeolite, Cu/ZrO2, TiO2-$ZrO_2$, Ru-RuOx/$TiO_2$, Ag,Cu/$TiO_2$, SiC, Cu/SiC, Rh complexes, Cu,Pt/N dopped $TiO_2$, $CdSe/Pt/TiO_2$ | Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons, | Roy [13] |
| $ZrO_2$, CdS, Ti-MCM, Ti silicalite molecular sieve, MgO, ZnO, $NiO/InTaO_4$ | Photocatalytic reduction of $CO_2$ over $TiO_2$ based catalysts | Kočí [14] |

***Table 3****: published research on complete oxidation of methane and/or short alkanes*

| **Title of article** | **Years** | **First author** | **Ref.** |
|---|---|---|---|
| Preparation in a hydrogen-oxygen flame of ultrafine metal oxide particles. Oxidative properties toward hydrocarbons in the presence of ultraviolet radiation | 1972 | Fromenti | [28] |
| Photointeraction on the surface of titanium dioxide between oxygen and alkanes (C2 - C8) | 1974 | Djeghri | [29] |
| Reactions of methane and ethane with hole centers $O^-$ | 1978 | Kaliaguine | [30] |
| Room temperature photo-activation of methane on titanium(IV) oxide supported molybdena | 1988 | Thampi | [31] |
| Methane oxidation at room temperature and atmospheric pressure activated by light via polytungstate dispersed on titania | 1989 | Graetzel | [32] |
| Selective photo-oxidation of light alkanes using solid metal oxide semiconductors ($CH_4$ produced a small amount of methanal together with $CO_2$) | 1993 | Wada | [33] |
| Preliminary Study on Photocatalytic Oxidation of $CH_4$ by $O_2$ on Water-Adsorbed Porous $TiO_2$ | 2000 | Chen | [34] |

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|---|---|---|---|
| Catalytic Activities of $MoO_3/TiO_2$ and $WO_3/TiO_2$ for Photocatalytic Oxidation of $CH_4$ by $O_2$ | 2000 | Chen | [35] |
| Photo-oxidation of short-chain hydrocarbons over titania (C2 - C6) | 2001 | Brigden | [36] |
| Kinetics of the Photocatalytic Total Oxidation of Different Alkanes and Alkenes on $TiO_2$ Powder | 2002 | Kleinschmidt | [37] |
| Photocatalytic oxidation on $TiO_2$ of methane from exhaust air of animal houses and liquid manure storages | 2003 | Melse | [38] |
| Photooxidation of methane over $TiO_2$ | 2004 | Lien | [39] |
| Sunlight-Assisted Photocatalytic Oxidation of Methane over Uranyl-Anchored MCM-41 | 2004 | Krishna | [40] |
| Part I: Photocatalyzed Total Oxidation of Olefines with Oxygen and Part II: Photocatalyzed Total Oxidation of Alkanes with Oxygen. | 2004 | Haeger | [41,42] |
| Kinetics and Mechanisms of Photocatalyzed Total Oxidation Reaction of Hydrocarbon Species with Titanium Dioxide in the Gas Phase | 2005 | Finger | [43] |

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|---|---|---|---|
| Photocatalytic degradation of methane under irradiation of vacuum ultraviolet light | 2006 | Liu | [44] |
| Decomposition of Halocarbons Using $TiO_2$ Photocatalyst<br>($CH_4$, $CCl_4$, $CHClF_2$) | 2006 | Wataru | [45] |
| Photocatalytic oxidation of low molecular weight alkanes: Observations with $ZrO_2$–$TiO_2$ supported thin films (C3 - C4) | 2006 | Twesme | [46] |
| Laboratory-scale photomineralisation of n-alkanes in gaseous phase, by photocatalytic membranes immobilising titanium dioxide (C1, C2, C7) | 2006 | Bellobono | [47] |
| Impact of a photocatalytic cover during the storage period of pig slurry on gaseous emissions ($CH_4$, $NH_3$, $N_2O$, $CO_2$) | 2006 | Espagnol | [48] |
| Influence of irradiance, flow rate, reactor geometry, and photopromoter concentration in mineralization kinetics of methane in air and in aqueous solutions, by photocatalytic membranes immobilizing titanium dioxide | 2008 | Bellobono | [49] |

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|---|---|---|---|
| Photocatalytic $TiO_2$ coating to reduce ammonia and greenhouse gases concentration and emission from animal husbandries ($CH_4$, $NH_3$, $N_2O$, $CO_2$) | 2008 | Guarino | [50] |
| Photocatalytic $TiO_2$ treatment effects on ammonia, greenhouse gases, dust concentration and emission in a weaning room ($CH_4$, $NH_3$, $N_2O$, $CO_2$) | 2008 | Costa | [51] |
| Photocatalytic Steam Reforming of Methane | 2010 | Shimura | [52,53] |

***Table 4**: Global Radiative Forcing and GWP$_{100}$ of some minor GHGs*

| some minor GHGs | Global Radiative Forcing in 2005 (W.m$^{-2}$) [81] | GWP$_{100}$ (lifetime yr) |
|---|---|---|
| HCFC-22 or $CHClF_2$<br>chlorodifluoromethane | 0.033 (1.2%) | 1700 (12) |
| CFC-113 or $CCl_2F$-$CClF_2$<br>Trichlorotrifluoroethane | 0.024 (0.9%) | 4800 (85) |
| HFC-134a or $CFH_2CF_3$<br>tetrafluoroethane | 0.0055 | 1430 (14) |
| PFC-14 or $CF_4$<br>tetrafluoromethane | 0.0034 | 5700 (50000) |
| HCFC-142b or $CH_3CF_2Cl$<br>chlorodifluoroethane | 0.0031 | 1800 (18) |
| $SF_6$<br>Sulphur hexafluoride | 0,0029 | 22800 (3200) |
| $NF_3$<br>nitrogen trifluoride | - - | 17200 (550) |
| *Total 15 minor GHGs*<br>CFCs +HFCs + PFCs + $SF_6$ | *0.092* | - - |

***Table 5**: selected articles, reviews or books about NOx and VOCs abatement or remediation*

| **Title** | **Publication year** | **1st Author** | **Ref.** |
|---|---|---|---|
| Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement | 2010 | Hassan | [168] |
| Conversion of nitrogen oxides on commercial photocatalytic dispersion paints. | 2010 | Laufs | [169] |
| Photocatalytic application of $TiO_2$ for air cleaning (Chapter 17) | 2010 | Anpo | [170] |
| Some views about indoor air photocatalytic treatment using $TiO_2$: Conceptualization of humidity effects, active oxygen species, problem of $C_1$–$C_3$ carbonyl pollutants | 2010 | Pichat | [171] |
| Photocatalytic purification of volatile organic compounds in indoor air: a literature review. | 2009 | Mo | [172] |
| $TiO_2$-based building materials: above and beyond traditional applications | 2009 | Guo | [173] |

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|---|---|---|---|
| Indoor air purification using heterogeneous photocatalytic oxidation | 2009 | Yu | [174] |
| Photocatalytic titania based surfaces: environmental benefits. | 2008 | Allen | [175] |
| Air purification by pavement blocks: final results of the research at the BRRC. | 2008 | Beeldens | [176] |
| Evaluation of titanium dioxide as a photocatalyst for removing air pollutants | 2008 | LBNL | [177] |
| Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art | 2007 | Wang | [178] |
| Comparative study on cementitious products containing titanium dioxide as photocatalyst | 2007 | Hüsken | [179] |
| Evaluation of photocatalysis for gas-phase air cleaning<br>Part 1: Process, technical and sizing considerations;<br>Part 2: Economics and utilization. | 2005 | Tompkins | [180] |
| Use of modern photocatalytic systems to clean the air from the industrial buildings of coke and coal chemicals plants | 2004 | Pershin | [181] |

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|---|---|---|---|
| Photocatalytic oxidation for indoor air purification a literature review | 2003 | Zhao | [182] |
| Photochemical purification of water and air | 2003 | Oppenländer | [183] |
| Ambient air treatment by titanium dioxide based photocatalyst in Hong Kong | 2002 | Yu | [184] |
| A critical review on studies of volatile organic compound sorption by building materials | 2002 | Zhang | [185] |
| Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air | 2001, 1999, 1997, 1995, 1994 | Blake | [118] |
| Heterogeneous photocatalysis for purification, decontamination and deodorization of air | 1997 | Peral | [186] |
| Environmental applications of semiconductor photocatalysis | 1995 | Hoffmann | [187] |
| Destruction of volatile organic compound emissions by photocatalytic oxidation: bench scale test results and cost analysis | 1995 | Turchi | [188] |

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|---|---|---|---|
| Photocatalytic purification and treatment of water and air | 1993 | Ollis | [189] |
| Photocatalysis and environment: trends and applications | 1988 | Schiavello | [190] |