A Short Review on Photocatalytic Degradation of Formaldehyde

Minoo Tasbihi[*, †], Joanna K. Bendyna, Peter H. L. Notten, and H. T. (Bert) Hintzen

Group Energy Materials and Devices, Department of Chemical Engineering and Chemistry,
Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands

Nowadays, it is a great challenge to eliminate toxic and harmful organic pollutants from air and water. This paper reviews the role of TiO_2 as a photocatalyst, light source and photoreactor in the particular case of removal of formaldehyde using the photocatalytic reaction by titanium dioxide (TiO_2) in aqueous and gaseous systems. The reaction mechanisms of the photocatalytic oxidation of gaseous formaldehyde are given. We also present a detailed review of published articles on photocatalytic degradation of formaldehyde by modified titanium dioxide doped with foreign species such as metal and non-metal components. We point out the most prospective developments of the photocatalyst compositions for the future potential commercial applications.

Keywords: Formaldehyde, Photocatalytic Degradation, TiO_2, Co-Doped of TiO_2.

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1. INTRODUCTION

In developed society, most people spend more than 80% of their time in closed environments like modern office buildings, shopping centers, schools and newly built houses and even at home or inside vehicles.[1–4] Moreover, it is possible that the concentration of many indoor pollutants is higher than those outside. This is caused by a quick release of contaminants of which the concentration builds up.[1]

Volatile organic compounds (VOCs) can be emitted from cooking, combustion, exhaust gases, tobacco smoke, furniture, building materials, and traffic pollutants.[5] In 1995, The US Environmental Protection Agency (USEPA) identified indoor air pollution as one of the top environmental risks.[2] Formaldehyde already was classified as a known human carcinogen (cancer-causing substance) by the International Agency for Research on Cancer and as a probable human carcinogen by the U.S. Environmental Protection Agency.[6] Among the many chemical contaminants usually found in polluted indoor air, formaldehyde (HCHO) is one of the major species.

Formaldehyde is a colorless gas with a strong, unpleasant odor. A long-term exposure to this toxic pollutant may cause health problems such as irritations and allergies, and is considered to be carcinogenic.[7] The sick building syndrome is one of these health problems, and is characterized by drowsiness, headache, sore throat and mental fatigue. Formaldehyde is produced by, for example: plants oxidizing methanol; as a by-product of other carbon compounds reacting with NO, O_3 or OH radicals in the air; exhaust gas of automobiles and aircrafts. Also, indoor sources such as isolation, flooring materials and smoking or cooking.[8] Therefore, there is a need for the development of air cleaning technologies.[4]

A number of studies have been made for removing formaldehyde from gas and liquid streams, including adsorption,[8–10] biological,[11] catalytic[12–14] and photocatalytic oxidation processes.[15]

The adsorption, biological and catalytic methods have drawbacks such as the need to operate at high temperature, the use of costly materials and the lacking efficiency of the catalysts. It is therefore necessary to investigate the

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[*]Author to whom correspondence should be addressed.
[†]Present address: Laboratory of Environmental Research, University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia.

use of efficient catalytic materials to remove formaldehyde in indoor or outdoor environment. Semiconductor heterogeneous photocatalysis is a widespread technique that has the great potential to remove organic contaminants in air or water.[15] This process which is in the group of "Advanced Oxidation Processes (AOPs)" is suitable for the oxidation and degradation of organic pollutants. Heterogeneous photocatalysis was developed in the 1970s for the elimination of toxic and bio–resistant organic and some of the inorganic compounds.[16] A highly attractive advantage of the heterogeneous photocatalytic treatment is that it is capable of decomposing many kinds of organic and inorganic compounds under ambient temperature conditions.[17] The process is also non-selective to a very broad range of reactants varying from organic compounds such as alkanes and alkenes, phenolic compounds, aromatics, organic acids, amines, cyanide and nitrite. Other advantages are: no additives are required since oxygen is readily available from the air, cheap chemicals can be used, total mineralization achieved for many organic pollutants, suitable for low concentration, possible combination with other decomposition methods (in particular biological), reactions taking place at room temperature and to save energy and reduce greenhouse gasses.[18]

In most cases, the semiconductors used as photocatalysts can be activated by sunlight which makes them economically competitive; otherwise they can be activated by UV or visible light irradiation. Many semiconductors such as TiO_2, ZnO, CdS, ZnS, SnO_2, Fe_2O_3, WO_3, etc., have been studied as photocatalysts.[19]
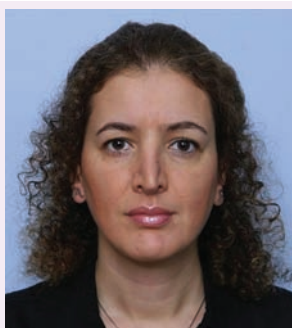
Minoo Tasbihi received her B.Sc. and M.Sc. in Chemical Engineering in 2000 and 2003, respectively. She worked as a research assistant in the Imam Hussein University in Iran for one year (2003–2004) and worked as a process engineer in the Petrochemical Company in Iran (2004–2005). She then worked as a research assistant in the University of Science Malaysia for two years (2005–2007). She received her Ph.D. in Environmental Science from the University of Nova Gorica, Slovenia in 2010. She was research assistant in the University of Nova Gorica. In 2011, she worked as a postdoctoral research fellow in the Eindhoven University of Technology in The Netherlands on joint industrial project between Philips Research Eindhoven and Eindhoven University of Technology. In 2014, she became an assistant professor in Chemistry in the University of Nova Gorica. Her current research subject is material design, different synthesis procedures and investigation of the physico-chemical properties of materials by using various characterization techniques, reaction engineering, photochemical oxidation (PCO) techniques, kinetics, design, construction and optimization of chemical reactors, modeling and optimization.

Joanna K. Bendyna was born in Poland in 1978, was educated in Chemical Engineering and Technology at TU Szczecin in Poland. In 2002 she received M.Sc. and Eng. for the complex organic synthesis of the pharmaceuticals. She continued as scientist till 2005 to work on novel catalysts for ammonia synthesis. In 2005 she became a scientist at Leibnitz Institute in Dresden in Germany to work on Ion-beam deposition of films. In 2009 she received Dr. rer. nat. in Chemistry for her work at Max Planck Institute on "New developments in nitridometalates and cyanamides." Till 2013 she worked as a researcher at TU Eindhoven in The Netherlands on novel photo-catalysts (with Philips), new hydrogen-storage materials; Li-ion batteries, and novel optical ceramics. In 2013 she became a research scientist at TNO to work on 3D printing of metamaterials, ALD for Photovoltaics, and photo- and electro-catalysts for the conversion of CO2. In 2014 she joined Empa in Switzerland as PI of her FP7 Marie-Curie Fellowship on "New Metal-Carbons." In 2015 she returned to TU Eindhoven. She was acknowledged as the organizer of symposiums at E-MRS 2014 and 2015 Fall Meetings. She gave over 20 invited talks as well as 30 conference presentations.

Peter H. L. Notten was born in The Netherlands in 1952, was educated in analytical chemistry and joined Philips Research in 1975. While working at these laboratories on the electrochemistry of etching of III–V semiconductors he received his Ph.D. from the Eindhoven University of Technology in 1989. Since 2000 he has been appointed as professor at the Eindhoven University of Technology where he is heading the group Energy Materials and Devices. In 2014 he has been appointed as International Adjunct Faculty at the Amrita University, Coimbatore, India and as scientific advisor at the Forschungszentrum Jülich, Germany. He is member of the Editorial Board of Advanced Energy Materials and International Journal of Electrochemical Science. He has published as (co)author about 200 scientific papers and contributions to scientific books and owns about 30 patents.

H. T. (Bert) Hintzen is associate professor in Optical Materials at Delft University of Technology (The Netherlands). He studied chemistry and physics (B.Sc., 1979) at the University of Nijmegen, graduated (M.Sc., 1982) on solid state physics and inorganic chemistry at the same university, and obtained his Ph.D. degree (1990) on luminescent materials at Utrecht University with Professor Dr. Blasse as supervisor. In the period 1982–1992 he worked at Philips Research and Philips Lighting Materials Laboratories Eindhoven. From 1993 till 2013 he was affiliated with Eindhoven University of Technology as associate professor on Energy Materials and Devices. In 1998 Bert Hintzen was visiting professor at Rennes University (France), in 2003 and 2007 Research Fellow at Tokyo University (Japan), and in 2013 Research Fellow at the National Institute for Materials Science (Japan). During the years 2009–2010 he was also appointed part-time professor in Sustainable Energy at Avans University of Applied Sciences (The Netherlands), and since 2014 he is visiting professor at Rowan University (USA). His research interests are concerned with the design, preparation, characterization, properties and applications of inorganic (ceramic, phosphor, pigment, photo-catalytic, lithium battery, hydrogen storage) materials, with emphasis on composition-structure-property relationships. Current research topics include spectral conversion materials for application in the field of energy (LEDs, solar cells) and mobility (smart highway). Bert Hintzen serves as associate editor of the Journal of the American Ceramic Society and is member of the editorial boards of the International Journal of Luminescence and Applications and the open-access journal Materials. He is (co-)author of more than 150 scientific publications and holds about 15 patents as (co-)inventor.

This paper presents the role of type of photocatalyst, light source and photoreactor on the removal of formaldehyde in particular, using the photocatalytic reaction induced by titanium dioxide (TiO_2) in aqueous and gaseous systems. The reaction mechanisms of the photocatalytic oxidation of gaseous formaldehyde are given. The main focus is on the visible-light active photocatalysts, as being the most proficient in saving energy since they may decompose hazardous VOCs just by using the sun light. Therefore, these seem to be the most promising to reduce greenhouse gases release compared to those working with artificial light sources powered by electricity still produced in a large part using fossil fuels which increase CO_2 level. The photocatalysts mostly were obtained by doping and co-doping with metal and non-metal ions.

2. TITANIUM DIOXIDE (TiO_2)

Titanium dioxide (TiO_2) is a natural occurring oxide of titanium; it is also known as titania or titanium (IV) oxide. In nature TiO_2 exists in five different crystalline forms, i.e., anatase, rutile, brookite, monoclinic, and orthorhombic. However, monoclinic and orthorhombic phases of TiO_2 are two exceptions found only in shocked granet gneisses from the Ries crater in Germany.[20] Anatase type of TiO_2 has a crystalline structure that corresponds to the tetragonal symmetry. Brookite type of TiO_2 has an orthorhombic crystalline structure. Rutile appears to be the most common form of TiO_2, while anatase and brookite forms of TiO_2 tend to convert into rutile form upon heating at high temperature.

The popularity of TiO_2 as a photocatalyst is due to its superior characteristics:
(a) It has environmentally friendly nature (i.e., non toxicity), low cost, chemical and thermal stability, high natural abundance.

(b) It promotes ambient temperature oxidation of major classes of indoor air pollutants under UV irradiation.
(c) Complete degradation of a broad range of pollutants by TiO_2 can be achieved under ambient operation conditions.
(d) No chemical additions are required during photocatalysis.[21]

TiO_2 is a versatile material that has applications in a wide assortment of products including paint, white pigments, plastic, inks, paper, sunscreen lotions, electrochemical electrodes, foodstuffs, pharmaceuticals and solar cells which in most of them it is not photocatalytically active and non-crystalline.[21–23]

Titanium dioxide has been extensively studied as a photocatalyst for the photocatalytic oxidation of organic compounds. A wide range of organic compounds can be oxidized to CO_2 and H_2O at room temperature on a TiO_2 photocatalyst in the presence of UV illumination.[13, 23] The photocatalytic activities of various forms of TiO_2, such as films,[1, 24] powders,[25, 26] nanorods,[27] nanofibers,[28] immobilized TiO_2[3, 28, 29] and doped TiO_2[30–32] have been evaluated through degradation of formaldehyde under light irradiation.

3. REACTION MECHANISMS OF PHOTOCATALYSIS

The ability to degrade organic and inorganic pollutants comes from the redox reaction initiated after photoactivation of the semiconductor material. A semiconductor (SC) material has an electronic band structure in which the highest occupied energy band is called the valence band (VB) and the lowest empty band is called the conduction band (CB). These bands are separated by a band gap which is in the order of electron volts.[33]

When a photon of energy higher or equal to the band-gap value of the semiconductor is absorbed by a particle, an electron from the VB is promoted to the CB with simultaneous generation of a photogenerated hole (h_{vb}^+) in the VB and photogenerated electron (e_{cb}^-) in the CB (Eq. (1)).[34]

A photochemical reaction is not assured only by photo-excitation of a semiconductor. An important thermodynamic requirement is the positioning of the donor and acceptor levels of the adsorbent that should be above and below the valence and conduction band of the semiconductor, respectively, to create a driving force for the photochemical reaction to take place.[35]

The general reaction mechanism of the hydroxyl-radical mediated photocatalytic reaction process is represented by the Eqs. (1)–(12). It applies to TiO_2, but also to other semiconductors with similar band-gap energies, and valence and conduction band positions. It must be noted that although both anatase and rutile TiO_2 absorb UV radiation, rutile TiO_2 can also absorb radiation that is nearer to visible-light because it has a narrower band-gap than anatase (3.0 vs 3.2 eV). Anatase TiO_2 exhibits a higher photocatalytic activity than rutile due to its conduction band position which exhibits stronger reducing power as compared to rutile TiO_2.

An electron paramagnetic resonance (EPR) study showed that the creation of a rutile-anatase interface can lead to enhanced photocatalytic activity. It is proposed that electron transfer from rutile to a lower lying anatase trapping site can separate the electron from the hole, which can then be transferred to sites on the surface. It is believed that this is an explanation of why the P25 Degussa, which is a combination of anatase and rutile, shows better photocatalytic activity than a pure anatase or rutile crystal.[36]

e_{cb}^- and h_{vb}^+ can recombine at the surface or in the bulk of the particle in a few nanoseconds (Eq. (8)) and the energy dissipates as heat. Alternatively, the charge carriers can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. Thereby, subsequent redox reactions can be initiated (Eqs. (2)–(4)).
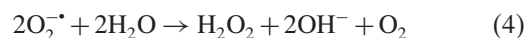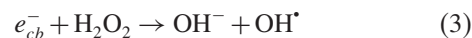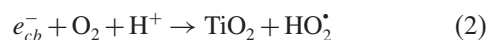
It is accepted that the initial step for photocatalytic degradation is the formation of an extremely reactive but short–lived hydroxyl radical (OH$^\bullet$) by hole trapping (Eqs. (5) and (6)). The OH$^\bullet$ is formed on the highly hydroxylated semiconductor surface. Hydroxyl species are formed when water interacts with bridging oxygen atoms on the surface, or when coordinating to oxygen vacancies.[35] This process is immediately followed by the reduction of adsorbed oxygen species, derived either from dissolved oxygen molecules, or by other electron acceptors available. The main reactions governing the photocatalysis process are as follows:

Electron–hole pair formation:

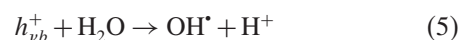$$TiO_2 + h\nu \rightarrow TiO_2 + e_{cb}^- + h_{vb}^+ \qquad (1)$$
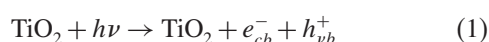
(Semiconductor valence band hole and conduction band electron)

Electron removal from the conduction band:

$$e_{cb}^- + O_2 + H^+ \rightarrow TiO_2 + HO_2^\bullet \qquad (2)$$

$$e_{cb}^- + H_2O_2 \rightarrow OH^- + OH^\bullet \qquad (3)$$

$$2O_2^{-\bullet} + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \qquad (4)$$

Hole trapping:

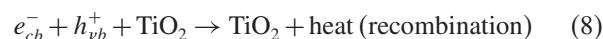$$h_{vb}^+ + H_2O \rightarrow OH^\bullet + H^+ \qquad (5)$$

$$h_{vb}^+ + OH^- \rightarrow OH^\bullet \qquad (6)$$

Oxidation of organic pollutant molecules:

$$OH^\bullet + O_2 + C_xO_yH_{(2x-2y+2)} \rightarrow xCO_2 + (x-y+1)H_2O \qquad (7)$$
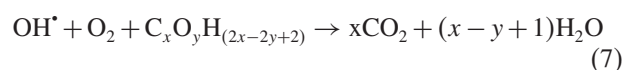
Non–productive radical reactions:

$$e_{cb}^- + h_{vb}^+ + TiO_2 \rightarrow TiO_2 + heat\,(recombination) \qquad (8)$$

$$2OH^\bullet \rightarrow H_2O_2 \qquad (9)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (10)$$

$$2OH^\bullet + H_2O_2 \rightarrow 2H_2O + O_2 \qquad (11)$$

$$OH^\bullet + HCO_3^- \rightarrow CO_3^{-\bullet} + H_2O \qquad (12)$$
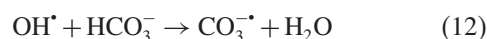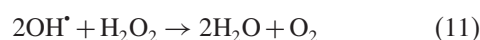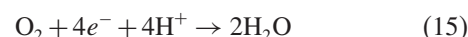
In general the major oxidative and reductive processes in the photodegradation of formaldehyde follow the Eq. (1) and further continue via oxidation:[24]

$$HCHO + H_2O + 2h^+ \rightarrow HCOOH + 2H^+ \qquad (13)$$

$$HCOOH + 2h^+ \rightarrow CO_2 + H^+ \qquad (14)$$

And reduction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (15)$$
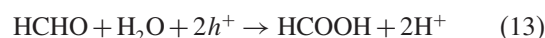
In detail the photolysis and photocatalysis of formaldehyde are as follows:
Photolysis of formaldehyde:[37]

$$HCHO + h\nu \rightarrow H + HCO^\bullet \qquad (16)$$

$$^\bullet CHO + HO_2^\bullet \rightarrow HOCH_2OO \qquad (17)$$

$$HOCH_2OO + HO_2^\bullet \rightarrow HOOCH_2OH + O_2 \qquad (18)$$

$$HOOCH_2OH \rightarrow H_2O + HCOOH \qquad (19)$$
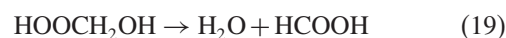
Photocatalysis of formaldehyde: The possible mechanisms of photocatalytic degradation of formaldehyde in aqueous phase[38] and gaseous phase follow the Eq. (1) and further continue:[39, 40]

$$H_2O \rightarrow H^+ + OH^- \qquad (20)$$

$$h^+ + OH^- \rightarrow OH^\bullet \qquad (21)$$

$$e^- + O_2 \rightarrow O_2^- \qquad (22)$$

$$HCHO + {}^{\bullet}OH \rightarrow {}^{\bullet}CHO + H_2O \qquad (23)$$

$${}^{\bullet}CHO + {}^{\bullet}OH \rightarrow HCOOH \qquad (24)$$

$${}^{\bullet}CHO + {}^{\bullet}O_2^- \rightarrow HCO_3^- \rightarrow H_2CO_3 \rightarrow HCOOH \qquad (25)$$

$$HCOOH \rightarrow HCOO^- \rightarrow H_2O + {}^{\bullet}CO_2^- \text{ or}$$

$$HCOO^- \rightarrow H^+ + {}^{\bullet}CO_2^- \qquad (26)$$

$${}^{\bullet}CO_2^- \rightarrow CO_2 \qquad (27)$$
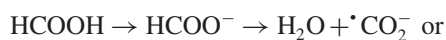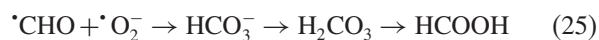
Formic acid is the most commonly found intermediate from the conversion of formaldehyde by photolysis and photocatalysis.

4. PHOTOCATALYTIC DEGRADATION OF FORMALDEHYDE

4.1. Photocatalyst

The photocatalytic activity of titania is restricted to UV light region due to its large band gap. Besides, massive recombination of photogenerated charge carriers leads to low photocatalytic efficiencies. The obstacles can be overcome by modifying the electronic band structure of titania and improving charge separation including different strategies like coupling with narrow band gap semiconductor, metal ion/non-metal ion doping, co-doping with two or more foreign ions, surface sensitization by organic dyes or metal complexes, and noble metal deposition.[34, 36] In particular, co-doping of titania leads to a significant synergistic effect compared to a single ion doping, often accompanied by reduction in the number of carrier recombination centers and enhancement of the desired visible-light absorption.[41, 42] Moreover, while designing efficient novel photocatalysts the effects of the structural charge balance and crystal lattice vacancies have to be considered.

Below the examples of various modified titania-based materials are listed and alternative photocatalysts are discussed, see Table I. The selected examples emphasize the latest developments on the visible-light active photocatalysts, photocatalysts efficiency, and clever implementation of photocatalysts into the tests and reactor systems.

4.1.1. Visible-Light Active Photocatalysts

A F–N–doped TiO$_2$ photocatalyst was synthesized by treatment of N–TiO$_2$ with NH$_4$F by an impregnation-calcination method.[43] The NH$_4$F treatment enhances significantly photocatalytic activity of N–TiO$_2$ and increases the visible-light absorption of N–TiO$_2$ photocatalyst. In detail, oxygen vacancies produced by previous nitrogen doping for N–TiO$_2$, can improve further nitrogen doping when N–TiO$_2$ is modified by NH$_4$F; while fluorine doping can remove the oxygen vacancies derived from the further nitrogen doping. Furthermore, with an increase of the calcination temperature, F$^-$ ions could be doped

into TiO$_2$ more easily. Thus, excessive F$^-$ ions could be doped into TiO$_2$ lattice at higher temperatures, which led to an increase of oxygen vacancy concentration instead of reducing the concentration. The photocatalytic activity of as-prepared photocatalysts was investigated towards the degradation of gaseous formaldehyde with a blue light-emitting diode (LED) as light source. This was possible because the absorption intensities of F–N–TiO$_2$ were observed between 400–535 nm. The preparation conditions such as the calcination temperature and the initial molar ratio of NH$_4$F to N–TiO$_2$, have a major influence on the photocatalytic activity.[43] The visible light absorption and the specific surface area were influenced by increase of the calcination temperature. F–N–TiO$_2$ photocatalyst achieved high formaldehyde removal of 87% after 15 h irradiation with a blue light.

Zhang and Liu[44] studied the visible-light-induced degradation of formaldehyde over N–Ni co-doped titania photocatalysts. The photocatalyst powders were prepared by the sol–gel method. The prepared N–Ni co-doped photocatalyst consisted only of anatase and the doping could retard the phase change. Since nitrogen atoms were incorporated into the structure of TiO$_2$ this led to a narrowing of the band gap of titania. The co-doped photocatalyst showed optical absorption and displayed photocatalytic activity under visible-light due to the observed absorption intensities between 400 nm to about 640 nm. The as-prepared photocatalyst had a porous surface. The annealing temperature and the doping amount of nitrogen and nickel had effects on the photocatalytic activity of the N–Ni co-doped photocatalyst. Compared with P25, there was an enhancement of almost 200% in photoactivity for the decomposition of formaldehyde under visible-light for the N–Ni co-doped photocatalyst calcined at 600 °C. The photocatalyst achieved high removal of formaldehyde of 80% after 2 h. The results revealed that the high visible activity of as-prepared photocatalyst was attributed to the synergistic consequence of several beneficial effects.

Liu et al.[27] synthesized monodispersed Fe-doped TiO$_2$ nanorod cluster nanoparticles by a modified hydrothermal and solvothermal method. They claimed that the Fe^{3+}-dopants in TiO$_2$ lattice not only lead to a significant extension of the optical response from the UV to the visible region but also diminish the recombination rates of the electrons and holes. The Fe^{3+}-dopant could not only participate as a temporary trapping site of photo-induced electrons[42, 43] but also function as a shallow capturing site of photo-induced holes,[44–46] which will competently separate the photo-excited electrons and holes and prolong their lifetime. In addition, according to the viewpoint of crystal field theory, the Fe^{3+}-dopant is more stable in the TiO$_2$ lattice because of its $3d^5$ (half-filled high spin) electronic configuration, so the captured electrons or holes can be easily released from Fe^{2+} or Fe^{4+} to regenerate Fe^{3+} and then migrate to the catalysts surface to initiate the

Table I. A summary of various studies on photocatalytic degradation of formaldehyde.

Photocatalyst	Preparation method	Excitation light	Initial formaldehyde concentration	Photoreactor type	Comments of the obtained results	Reference
N–TiO$_2$ coated on glass F–N–TiO$_2$ coated on glass	Impregnation-calcination	Blue light-emitting diode (blue LED)	1600 ppm gaseous (20 ml gaseous)	Cylindrical	87% of formaldehyde removal for 15 h irradiation; absorption intensities : 400–535 nm	[43]
N–Ni co-doped TiO$_2$ powder	Sol–gel	500 W Xenon with a 400 nm glass cut filter to remove UV light (Visible)	9.824 ppm gaseous	Cubic	80% of formaldehyde removal for 2 h irradiation; absorption intensities between 400 nm to about 640 nm	[44]
Fe–TiO$_2$ nanorod cluster	Modified hydrothermal and solvothermal	Visible light	2500 ppm liquid	Cylindrical	10.5 times higher formaldehyde removal compared to P25; absorption intensities: 400–600 nm	[27]
Ag/InVO$_4$–TiO$_2$ composite thin film	Sol–gel	Visible light	–	Cylindrical	50.3% formaldehyde removal after 10 h; edge of the absorption observed at 600 nm	[49]
TiO$_2$ and Cr/TiO$_2$ thin film	Sol–gel	250 W-metal Halide light (solar light)	400 ppm gaseous	Single-plate Parallel-plate	Cr/TiO$_2$: formaldehyde degradation effect–percentage reduction of formaldehyde-was 18%; absorption band was extended to the visible range	[50]
N–TiO$_2$ powder, N–Fe–TiO$_2$ powder, N–Fe–WO$_3$–TiO$_2$ powder	Sol–gel combined impregnation	UVA	250 mL liquid	Cylindrical	Formaldehyde removal of N–Fe–WO$_3$–TiO$_2$ was 77.6%; absorption extended to the visible-light	[31]
TiO$_2$/Ti wire net, Pd–TiO$_2$	Sol–gel dip coating	UV$_{254nm}$ UV$_{254+185nm}$	450 ppbv gaseous	Continuous flow mode	Conversion of formaldehyde was about 85% on Pd-TiO$_2$; no absorption data available	[32]
Ag/TiO$_2$ coated on the glass plates or sticks	Impregnation	UVLED, UVC, UVA, TG Purple Hi LED	500 ppmv gaseous	Cylindrical	Decomposition efficiency of formaldehyde using 40 UVLED after 7 h was 95%; no absorption data available	[29]
Millennium PC105 coated on white Portland Cement (commercial)	–	High-medium pressure mercury lamp with optical filter (transmittance: $\lambda > 280$ nm)	20 ppm gaseous	Dynamic flow (cylindrical-shape chamber)	Formaldehyde removal fluctuates between 40% and 65%; absorption at typical UV-range	[52]
Continuous TiO$_2$ fiber	Sol–gel	UVC (25 W)	10 mg/L with the pH = 5.0 (liquid)	Cylindrical	Formaldehyde removal of 98.6%; no absorption data available	[53]
TiO$_2$/tourmaline composite	Sol–gel	UVA (15 W, $\lambda = 365$ nm)	1.43 μL/L (liquid)	Cubic chamber	Formaldehyde removal of about 90%; absorption edge at about 435 nm	[54]

photocatalytic reactions. On the other hand, Fe^{3+}-dopant effectively extends the UV-vis spectra of TiO_2 into visible-light region. The absorption edge revealed the red-shift effect with the absorption intensities observed between 400–600 nm. The photocatalytic activity was evaluated by photocatalytic decomposition of formaldehyde in air under visible-light illumination. The well-controlled microstructure and morphology enhance the specific surface area of the Fe-doped TiO_2 photocatalyst compared with P25 and N-doped TiO_2 nano particles. The high photocatalytic activities of the Fe-doped photocatalysts have been ascribed to the enhanced specific surface area, visible-light response and diminished recombination rates of the photoexcited carriers. The Fe-doped TiO_2 photocatalyst revealed over 10 times higher degradation rate constant compared to P25 photocatalyst. This can be partially explained by typical very low activity of P25 under visible-light since it is UV active.[47, 48]

Ge et al.[49] synthesized novel $Ag/InVO_4$–TiO_2 composite thin films via a sol–gel method in order to investigate their visible-light-driven photocatalytic performance. The $Ag/InVO_4$–TiO_2 thin films extend the light absorption spectrum toward the visible region. The following edges of the absorption for the modified titania could be observed: 470 nm (Ag/TiO_2), 560 nm ($InVO_4$–TiO_2), and 600 nm ($Ag/InVO_4$–TiO_2). The photocatalytic activity of thin films was investigated in the decomposition of gaseous formaldehyde and methyl-orange in an aqueous solution at ambient temperature. The removal of formaldehyde of the $Ag/InVO_4$–TiO_2 thin films achieved 50.3% after 10 h while the removal of methyl-orange was about 45%. The photocatalytic results show that Ag doping can effectively enhance the photoactivity of $Ag/InVO_4$–TiO_2 thin films. CO_2 and SO_4^{2-} were detected as products of the decomposition of formaldehyde and methyl orange, respectively, indicating that formaldehyde and methyl-orange were completely oxidized over the $Ag/InVO_4$–TiO_2 films under visible-light. The Ag-doped ions were claimed to be responsible for surface electron trapping separating the charge carriers.

Lam et al.[50] built a visible-light-assisted photocatalytic glass reactor by parallel borosilicate glass plates coated on the upper surfaces with sol–gel TiO_2 thin films implanted with chromium (Cr) ions. The absorption band of these samples was extended to the visible range. The performance of the photocatalyst was measured in terms of its photocatalytic degradation of gaseous formaldehyde. The photocatalytic degradation effect–percentage reduction of the formaldehyde–calculated for the best Cr/TiO_2 sample was 18%. The results show promising usage of light transmitting glass substrate to allow transmission and distribution of light from an external source to achieve solar photocatalysis. They claimed that the number of parallel Cr/TiO_2-coated glass plates and the amount of Cr ion loading are the important parameters to maximize the efficiency of the use of solar irradiation. It was shown that the

amount of Cr ion has to be controlled properly due to the fact that each Cr/TiO_2-coated glass plate absorbs a portion of the incident light for its photocatalytic activation and allows light transmission available for the remaining coated plates.

Tong et al.[31] have synthesized TiO_2 photocatalysts doped with N, Fe and compounded by WO_3 via a sol–gel method combined with the impregnation method. Degradation of formaldehyde was used to investigate the catalytic activity. The maximum formaldehyde removal of 77.6% was more than 8 times higher compared to pure anatase TiO_2 over 180 min. They discussed that through the calcination procedure, TiO_2 and N could form $TiO_{2-x}N_x$ thus a new energy band which narrows the band gap of TiO_2 can been established. While regarding the impact of doping Fe^{3+}, it was supposed that Fe^{3+} can capture photoproduced electrons, and reduces the recombination of photogenerated electrons and holes and also extends the average life of the holes, which is beneficial to improve the photocatalytic activity. Furthermore, they concluded that Fe^{3+} can be electron captured, as the energy levels of Fe^{2+}/Fe^{3+} and Ti^{3+}/Ti^{4+} are slightly close, and thus the captured electron can easily migrate to the neighboring Ti^{4+} and then to the solid surface. They have shown that the optimal Fe content is 0.5 mol% and so when the content of Fe was lower than its optimal ratio, Fe would be a separation center. While when the content of Fe was higher than that, Fe would function as a recombination center and then the photocatalytic activity could be decreased. As regards the role of compounded WO_3 it was discussed that the mole fraction of WO_3 to TiO_2 is a key in the photocatalytic activity test. When the mole fraction of WO_3 to TiO_2 is about 2%, WO_3 would form a single layer on the TiO_2 surface. A suitable quantity of WO_3 compounding would help the separation of photoproduced electron–hole pairs and make more efficient the transportation of carriers, also improving the photocatalytic activity of the photocatalyst. On the other hand, when in the presence of an excess of WO_3 on the surface of TiO_2, the transfer center will become an electronic recombination center, and this would decrease the separation efficiency of the photoproduced electrons and holes, and reducing the photocatalytic activity of TiO_2.[51]

4.1.2. Surface, Morphology and Composite Modifications of UV Active Photocatalysts

The performance and mechanism of palladium modified TiO_2 films in the simultaneous decomposition of formaldehyde and ozone (O_3) by-product were investigated by Fu et al.[32] Pd nano-particles were deposited via an electrostatic self-assembly method. Modification of TiO_2 with Pd could increase the conversion of formaldehyde and O_3, particularly at the high relative humidity (RH) level, showing superb moisture-resistance performance. The highest observed conversion of formaldehyde and O_3 was about

85% and 74%, respectively. The results indicate that the $UV_{254+185\ nm}$ photocatalysis has a higher degradation rate of formaldehyde and longer lifetime (>30 h) of photocatalyst compared to common photocatalysis ($UV_{254\ nm}$) and catalyst deactivation was not observed. Because of a high electron affinity of the formed PdO_2, the photogenerated electrons could be trapped by PdO_x, and consequently the separation of e^-/h^+ pairs can be improved. As the reduction of PdO_2 and oxidation of PdO coexisted, the PdO_x could be dynamically stabilized, thus the photoactivity of Pd–TiO_2 was increased. Under $UV_{254+185\ nm}$ irradiation, the ozone might be decomposed on the Pd–TiO_2 via two different paths, i.e., photocatalytic reduction of O_3 in the presence of TiO_2 and decomposition of O_3 on PdO_x particles involved UV irradiation and trapped electrons.

The surface modification of Ag/TiO_2 coated on glass sticks and glass plates and photocatalytic decomposition of formaldehyde under UVLED light were studied by Shie et al.[29] The photocatalytic decomposition of formaldehyde at different initial concentrations was explained in accordance with the Langmuir-Hinshelwood model. The decomposition efficiency depended on the light-illumination which was measured for UVA, UVC and UVLED after 7 h with Ag/TiO_2 coated on glass plates and resulted in 86, 82, and 65%, respectively. The highest decomposition efficiency of Ag/TiO_2 coated on glass sticks using 40 UVLED measured after 7 h was 95%. The results demonstrate the feasible and potential use of UVLEDs in photocatalysis application. The light sources of UVLED (600 and 800 mW) can save a lot of energy in comparison with the traditional UV lamps (12 and 16 W). Using UVLED light as a light source can enhance not only the safety with less UV intensity but also the energy usage efficiency.

A clever implementation of the photocatalyst in a real life products was proposed by Hadj Aïssa et al.[52] who added anatase titania, PC-105 from Millennium Chemicals, to white Portland Cement to study the photocatalytic self-cleaning of mortars and concretes for removal of volatile organic compounds present in indoor and outdoor air. Recently, the concept of the self-cleaning concretes attracts significant attention of the industry. In the study, formaldehyde was selected as a representative VOC air pollutant. The photocatalytic removal of formaldehyde was carried out in a dynamic flow reactor with an in-line photoacoustic analytic spectrometer. The removal of formaldehyde in this cementitious matrix was fluctuating between 40% and 65%. The amount and distribution of titania was studied by Raman spectroscopy mapping and UV-vis diffuse reflectance spectroscopy at the exposed surface of the mortar sample. It was concluded that besides the photocatalytic self-cleaning properties of such cementitious materials, the atmospheric VOCs can also perhaps be removed from the surroundings. However, the surface properties of mortars and concretes allowed concluding that formaldehyde, its intermediate the formic acid and the

final product CO_2 can be also absorbed, so removed, by the surface. The complexity of the cementitious matrix leads to the conclusion that the mortars and concretes are in constant interactions with the atmosphere and they absorb the formaldehyde, intermediates and CO_2 on the surface. So, it was suggested that the formaldehyde removal was due to two processes: catalysis and photocatalysis. A morphology modification of the catalyst was proposed by You et al.[53] who synthesized continuous TiO_2 fibers by sol–gel method using titanate sol as a precursor. In the sol when the pH value is 5, the sol with the chain-like structure presents good spin ability with the initial molar ratio $R \leq 2$ ($R = H_2O$:TBOT (tetrabutyl orthotitanate), molar ratio). The titania fibers have the length of several meters and the diameter of about 30 μm. These are composed of crystals containing both anatase and rutile phase as nano-particles of high crystallinity. The continuous TiO_2 fibers show excellent stability for multiple reactions. The removal of formaldehyde was 98.6% which is higher compared to the 78.1% obtained with P25. After repeating 10 times the photocatalytic reaction the fibers have shown the degradation ratio of 90%.

TiO_2 supported tourmaline composites synthesized by the sol–gel method were prepared by Zhang and Qin.[54] The composites were used as a photocatalyst for photocatalytic degradation of formaldehyde. Tourmailene is a borosilicate mineral that belongs to trigonal space group R3m. One of the most important properties of tourmaline is the spontaneous and permanent poles, which can produce an electric dipole. The electrostatic poles that exist on the surface of the tourmaline crystals could improve the photocatalysis by inhibiting the recombination of electrons and holes produced by TiO_2. The results indicate the mixed-phase of anatase and rutile in the TiO_2/tourmaline composites. The TiO_2/tourmaline composites exhibited 6 times higher photocatalytic activity than pure TiO_2. The composites achieved the formaldehyde removal of about 90%. The outstanding photocatalytic activity of composites was maintained after 5 photocatalytic cycles. The characteristics of tourmaline, mixed phase of anatase and rutile, mesoporous structure, and large specific surface area could be the reason for the high and stable photocatalytic activity.

4.2. Light

The potential use of ultraviolet light emitting diodes (UVLED) in order to replace the traditional ultraviolet (UV) lamp for photodegradation of formaldehyde was investigated by Shie et al.[29] The UVLED, similar to other LEDs, has several advantages: has lower power, lower electromotive force (emf) demand and lower price, while higher efficiency, higher life-span and better security as compared to UV lamps.[28, 37, 41, 55] Also it does not generate heat.

Shie et al.[29] were tested various lamps including UVC (Philips TUV, 16 W), 365 nm UV lamp (UVA) (Philips,

12 W) and 30 or 40 UVLEDs (20 mW per UVLED, $\lambda = 383$ nm ($\Delta\lambda = 18$ nm), TG Purple Hi LED E1L5M-4P0A2-01, Toyota Gosei Co. Ltd., Taiwan). The photocatalyst used in this study was Ag/TiO_2 coated on the glass plates or sticks (for details see above, the chapter 4.1). The results show that the formaldehyde conversions using Ag/TiO_2 coated on glass sticks with different light sources are all higher than those of the glass plates because of the increase of illuminated area and the mass of Ag/TiO_2. Regarding the effect of light sources, UVLED were arranged in 3 lines or four lines (30 or 40 UVLED lights) in the center of the reactors surrounded by the quartz glass. The form of one UVLED is cone radiation, therefore, the distribution of light is in line direction and the illumination angle is not wide enough. The effecting illuminating area is far smaller than that of traditional UV lamp. The effective illuminating area of one UVLED is 1.76 cm^2, hence, the total effective irradiative areas of 30 and 40 UVLEDs are 52.8 and 70.4 cm^2, respectively. The total formaldehyde conversion with 30 and 40 UVLEDs after 7 h reaction time are 94% and 95%, respectively. The total power of 30 (600 mW) and 40 (800 mW) UVLEDs are far lower than those of 16 W UVC and 12 W UVA. In fact using UVLED (600 and 800 mW) has some advantages such as low energy consumption, longer life time, smaller size, higher energy usage efficiency, more safety with less UV intensity.[29]

Li et al.[43] investigated the photocatalytic degradation of formaldehyde under a group of blue LEDs ($\lambda_{max} =$ 458 nm, Latticepower Co., Ltd, China) as a light source in the presence of highly active F-N-doped TiO_2 photocatalyst (see Section 4.1). The results show that the photocatalytic degradation of formaldehyde cannot take place under pure TiO_2 photocatalyst film as TiO_2 is not able to absorb blue light. However, N-doped TiO_2 photocatalysts

exhibit obvious visible light activities for photocatalytic degradation of formaldehyde.
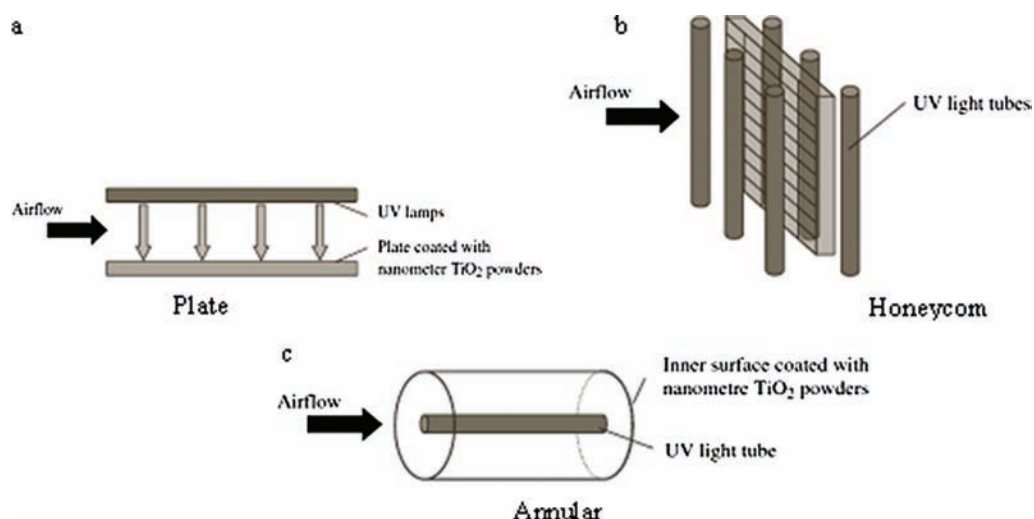
4.3. Photoreactor

The overall photocatalytic degradation of contaminants can be divided into five independent steps:
(1) Mass transfer of the organic contaminant(s) in the bulk phase to the TiO_2 surface.
(2) Adsorption of the organic contaminant(s) onto the TiO_2 surface.
(3) Photocatalysis reaction for the adsorbed phase on the TiO_2 surface.
(4) Desorption of the intermediate(s) from the TiO_2 surface.
(5) Mass transfer of the intermediate(s) from the interface region to the bulk fluid.[56]

As a result, the mass transfer rate, the kinetic reaction rate and the reaction surface area are the parameters which depend on the pollutant, the photocatalyst structure, composition and the operating condition as well as the important parameters of photoreactors.[56] A variety of photoreactors are reported in the literature, such as: power layer,[40] plate,[57, 58] honeycomb,[59] annular,[60] packed-bed,[61] fluidized-bed,[62] optical fiber,[63] combined-adsorption type[64] and mop fan.[65]

In the lab studies plate, (a), annular, (b) and honeycomb, (c) photoreactors (Fig. 1) are often applied for photocatalytic reactions.[56]

The reactors are sorted according to the configuration of the UV lamps with respect to the reaction area. The different configurations lead to different characteristics of the reaction area, mass transfer and photocatalytic reaction. For the plate type reactor, a large mass transfer and reaction rate can be obtained, but the reaction area is much smaller than for the other types of reactors. The UV light

Figure 1.   Representation of different photoreactors, (a) Plate, (b) honeycomb, (c) annular. From [56], J. Mo, et al. *Indoor Air.* 15, 291 (**2005**). © 2005, Blackwell Munksgaard.

is parallel to the reaction area, in the honeycomb monolith type reactor, (Fig. 1(b)), which results in low reaction rate even if the reaction area and mass transfer are large. For the annular type reactor, the mass transfer rate and reaction area are small, even when the UV light irradiates the reaction area directly (Fig. 1(c)).

Under ideal conditions, the structure of the photoreactor should have a high specific surface area, support small pass-through channels and low air velocity for the high mass transfer and have direct UV irradiation on the reactive surface. Normally, the structure of a photoreactor consists of two parts (a) the reactor, and (b) the UV-source. Most photoreactors have separate sources and the reactor which leads to the photocatalytic reaction being limited by either mass transfer or kinetic reaction. Based on this the removal efficiency is low and the reaction is incomplete.[56]

5. CONCLUSIONS

This paper reviewed studies addressing the photocatalytic removal of formaldehyde from aqueous or gaseous media using titanium dioxide based photocatalysts. Various sources emitting formaldehyde in the environment have been briefly discussed. The effects of metal and non-metal dopants and other modifications of TiO_2, such as morphology, surface, and composite formation on the efficiency of this specific photocatalytic reaction have also been reviewed. It can be concluded that the addition of selected dopants to pure titanium dioxide can significantly enhance the catalyst performance because it introduces intraband states that narrow the band-gap, shifting the adsorption of light into the visible region and may improve separation of the charge carrier's. Increasing the life time of the photocatalyst by the addition of antenna-like coupled semiconductors was also possible. Several attractive visible-light active photocatalysts showing relative high efficiency, which depends on the photocatalyst used for a comparison and the set-up of the experiment, were presented and compared in the form of a table. Interesting examples of the UV active modified TiO_2 photocatalysts, having improved efficiency compared to pure TiO_2 and capable of working under energy-saving light like UVLED, were also given. However, according to the available data the authors were using various techniques and the following experimental variables have to be considered when comparing these modified photocatalysts: various light sources, formaldehyde concentration, reactor type, test module of the photocatalyst (implementation of it in the set-up, e.g., bulk particles, thin film, or glass plates), amount of the photocatalyst, humidity level, and the reaction environment (gas vs liquid (here pH levels)). Therefore, too many variables of the presented findings led us to conclude that the reliable comparison on the performance of different photocatalysts is not possible. The advantages of UVLED lights in comparison with UV lights for photocatalytic degradation of formaldehyde were described. Furthermore, various types of photocatalytic reactors which were used for photocatalytic degradation of formaldehyde were shortly discussed.

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