



# Modified TiO<sub>2</sub> based photocatalysts for improved air and health quality



Vassilios Binas<sup>a, b, \*</sup>, Danae Venieri<sup>c</sup>, Dimitrios Kotzias<sup>d</sup>, George Kiriakidis<sup>a, b</sup>

<sup>a</sup> Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, P.O. Box 1527, 71110 Heraklion, Greece

<sup>b</sup> Crete Center for Quantum Complexity and Nanotechnology, Department of Physics, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece

<sup>c</sup> School of Environmental Engineering, Technical University of Crete, GR-73100 Chania, Greece

<sup>d</sup> Joint Research Centre, Institute for Health and Consumer Protection, Via Germania 29, Ispra, 21027 VA, Italy

## ARTICLE INFO

### Article history:

Received 5 October 2016

Received in revised form

31 October 2016

Accepted 6 November 2016

Available online 23 November 2016

### Keywords:

Photocatalysis

Indoor air quality

Visible light photocatalyst

Disinfection

## ABSTRACT

Photocatalysis with modified titania is a promising approach to improve both air and health quality. Modified titania with novel photocatalytic properties under indoor light irradiation leads to smart coatings, which are benchmark materials suitable for their indoor applications. It is generally accepted that the photocatalytic activity is affected by the light absorption, charge creation/recombination rate and surface reactivity. In this contribution we focus on modified TiO<sub>2</sub> as catalyst in heterogeneous photocatalytic processes and address the efficiency of TiO<sub>2</sub>-based building and construction materials on the removal of environmental pollutants indoors and outdoors. We also present data on the presence of eventually formed, toxicologically relevant and harmful by-products as the result of the photo-induced degradation of pollutants in an effort for better evaluation of induced risks for human health from the application of TiO<sub>2</sub> modified materials. Finally, we present recent results on the disinfection performance of these material and the inactivation of severe pathogens contained in water and indoor air environments.

© 2016 The Chinese Ceramic Society. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## Contents

1. Introduction .....	3
2. Photocatalysis on titania .....	4
2.1. Fundamentals of heterogeneous photocatalysis .....	4
2.2. Electronic, structural and physicochemical studies on titania (TiO <sub>2</sub> ) .....	6
3. Strategies for improving titania photoactivity with transition metal doping for visible light applications .....	7
4. Applications of modified TiO <sub>2</sub> for improved air and health quality .....	8
4.1. Air quality .....	8
4.2. Disinfection .....	11
5. Conclusions .....	13
6. Future trends in photocatalysis .....	14
Acknowledgements .....	14
References .....	14

## 1. Introduction

Heterogeneous photo-catalytic processes using semiconductor oxides such as TiO<sub>2</sub>, ZnO and WO<sub>3</sub> as photocatalysts are a promising technology and an efficient way for the removal of pollutants.

\* Corresponding author. Crete Center for Quantum Complexity and Nanotechnology, Department of Physics, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece.

E-mail address: [binasbill@iesl.forth.gr](mailto:binasbill@iesl.forth.gr) (V. Binas).

Peer review under responsibility of The Chinese Ceramic Society.

Moreover, they stand out among Advanced Oxidation Processes (AOPs) as promising and effective biocidal techniques for the purification of air and aqueous matrices [1]. According to the World Health Organization (WHO), air pollution possesses the sixth place among the leading causes of death globally [2]. Disease-causing microorganisms, which can be found in indoor and water environments, are the primary “target” of disinfection techniques, with the aim to control their concentration to tolerable and safe limits for public health protection [3]. Statistical air pollution performance measures play a major role in the model validation by comparing the observations with the modeled predictions. Recent statistical data for outdoors/indoors mainly refer to air pollution assessment and evaluation of the health effects that particulate matter (PM) of 2.5 microns that penetrate to deep lung and related polluting gases such as Ozone, NO<sub>2</sub>, SO<sub>2</sub>, CO, etc. Statistical models such as the longitudinal applied by the John Hopkins and Washington University team in 2006 [4] have demonstrated the development of asthma among children and vulnerable members of our society. However, a comprehensive set of ranked performance measures for validating the newly developed air quality models is still lacking. The rapid and easy spreads of pathogenic microorganisms in aerosols, through the consumption of contaminated water, illustrate the importance of their effective inactivation, including bacteria, viruses and protozoa [5].

In the case of photocatalytic materials such as TiO<sub>2</sub>, the process is triggered by the irradiation with UV light which leads to the promotion of electrons (e<sup>-</sup>) from the valence band to the conduction band leaving positive holes (h<sup>+</sup>) behind. The characteristic time for this step is a few femtoseconds. Produced positive holes and free electrons may subsequently either recombine-within nanoseconds- or diffuse to the semiconductor surface. In the latter case, the positive holes and electrons at the semiconductor/air interface, as very reactive species, can be trapped by adsorbed molecules of oxygen and water forming the high reactive hydroxyl radicals (OH•) and superoxide radicals (O<sub>2</sub>•-), which subsequently initiate redox processes leading to the degradation/mineralization of adsorbed organic and inorganic compounds [6–8].

TiO<sub>2</sub> is generally accepted as one of the most effective photo-induced catalysts and is frequently used to oxidize organic and inorganic compounds in air and water due to its strong oxidative ability and long-term photo-stability. TiO<sub>2</sub> is also a very common, non-expensive and non-toxic material. It exists in three crystalline structures; anatase, rutile and brookite. Anatase and rutile belong to the large bandgap semiconductors with bandgap energies of 3.2 and 3.0 eV, respectively. Anatase is basically the polymorph phase which has widely been used in photo-catalytic processes for depollution purposes. However, it has been indicated that mixtures of anatase and rutile are photo-catalytically more active than pure anatase or rutile phases of TiO<sub>2</sub> separately [9].

TiO<sub>2</sub>-based photo-catalytic materials and coatings when used as an outer layer on buildings facades in highly traffic roads have shown efficiency to degrade priority air pollutants (e.g. NO, NO<sub>2</sub>) originated from traffic exhausts. TiO<sub>2</sub>-containing paints have been tested in order to verify their effectiveness in removing NO under controlled environmental conditions of humidity, temperature and illumination (environmental chamber testing). NO was selected as the target pollutant, as it is one of the prominent pollutants in indoor and outdoor environments [10].

Apart from the mineralization of organic and inorganic substrates, TiO<sub>2</sub> photo-catalyst may trigger off the destruction of a wide range of microorganisms [11]. The beneficial action of photocatalysis relies primarily on the in situ generation of highly reactive species, like hydroxyl and superoxide radicals, as mentioned above, which induce oxidative stress to microorganisms causing their ultimate inactivation [1]. These reactive species when in contact with

microbial cells cause deleterious alterations in cellular structure, microbial inactivation and possible destruction [12]. Photo-catalytic disinfection has extensively been exploiting to control indoor air quality, an issue of major public health concern. Some examples include filters from heating, ventilation and air conditioning systems coated with TiO<sub>2</sub> to inactivate aerosolized *Escherichia coli*, lamps emitting visible or UV light coated with TiO<sub>2</sub> to inactivate *Staphylococcus epidermidis* and *Aspergillus niger* spores in flow chambers and a photo-catalytic scrubber to control *Enterococcus faecalis* and infectious bursal disease virus associated with livestock houses [13–15].

However, since UV represents a small part, only 5–8%, of the solar radiation, there is a need to find photo-catalysts, which are working/activated using light from the visible spectral region i.e. utilizing wavelengths between 380 and 500 nm, to profit of a greater amount of energy available from the solar radiation. In this context, in the past years significant efforts have been made to improve the catalytic activity of semiconductor oxides using visible light by modifying characteristics such as their specific surface area and energy band gap (E<sub>g</sub>).

This has been achieved, on the one hand, by using semiconductor oxides at nanoscale, hence increasing substantially the specific surface area and thus the number of reactive sites available, and, on the other, by doping. In particular, doping of TiO<sub>2</sub> with non-metal (C, N, S, I) and metal ions (Cr, Mn, Fe, Ni) is a feasible way to reduce its band gap and thus extend the photo-catalytic response of TiO<sub>2</sub> into the visible region of the solar spectrum. The addition of a dopant modifies the electronic structure of TiO<sub>2</sub> lowering its band gap either by increasing the valence band and/or by decreasing the conduction band energy shifting its absorbance into the visible light region (bathochromic shift-red shift) [16].

Due to the large surface/room-volume ratio indoors, the use of paints with air purifying potential is a very promising application in indoor environments considering that often pollution levels by far exceed those found outdoors. Moreover, the fact that humans spend approximately 90% of our time indoors underlines the importance photo-catalytic paints with de-polluting properties might have on our daily life by reducing human exposure to air pollutants indoors.

In the last decade extensive efforts have been focused onto the application of smart photo-catalytic materials and coatings, which could improve the quality in indoor environments too. In this context, among others, Mn-doped anatase TiO<sub>2</sub> photo-catalyst powder was successfully applied for the oxidation of NO under indoor-like illumination conditions. Results from these experiments demonstrated that, upon selection of the appropriate dopant and concentration, the photo-assisted elimination of air pollutants may be proved as a promising technique for remediation purposes in indoor environments too [17].

The present review provides selected information on TiO<sub>2</sub> as catalyst in heterogeneous photo-catalytic processes and is addressing the efficiency of TiO<sub>2</sub>-based building and construction materials for the removal of environmental pollutants in indoor and outdoor environments. Moreover, it includes information on the determination of eventually formed, toxicologically relevant by-products from the photo-induced degradation allowing a better evaluation on induced risks for human health from the application of TiO<sub>2</sub> modified materials.

## 2. Photocatalysis on titania

### 2.1. Fundamentals of heterogeneous photocatalysis

Photo-induced reactions in the heterogeneous phase proceed differently from those in the homogeneous phase. Due to the

interaction between the functional groups of the adsorbed chemical compounds and the adsorbent surfaces, bond lengths and bond angles between individual atoms of the adsorbed compounds are altered. This leads to changes in the absorption behavior of the compounds. Changes in absorption behavior are generally of a bathochromic nature (red-shift). In addition changes in the relative intensities of the individual bands (hyperchromic effects) might also be very important. As a consequence, compounds which practically do not absorb i.e. tropospheric light ( $\lambda > 290$  nm), once they are adsorbed on surfaces, demonstrate the ability to be transformed or degraded due to changes in the absorption behavior and the reaction with very reactive radicals formed on the catalytic surface. The catalytic effectiveness of a surface is measured by its ability to enable electron transitions and to inhibit fast recombination of charge carriers. Irradiation of a surface with UV and in some cases with visible light often leads to a change of the distribution of the charge carriers in/on the catalytically active surface.

There are many studies indicating the degradation of organic compounds (photomineralization) adsorbed onto e.g. silica gel by irradiation with sunlight or artificial light with  $\lambda > 290$  nm, which otherwise, as in the homogeneous phase, would not be transformed/degraded under the same reaction (irradiation) conditions. In some of these studies an attempt was made to correlate the rates of photo-oxidation (photomineralization, %CO<sub>2</sub> production) of environmental chemicals adsorbed onto silica gel with their ionization potential [18].

Over the last decades, heterogeneous photo-catalysis with the use of semiconductor oxides, such as TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, activated by UV light, found the interest of many research groups, in particular for the removal of organic and inorganic compounds in gas phase and aqueous systems [19–21].

Among these, TiO<sub>2</sub> is the most frequently used photo-catalyst due to its strong oxidative ability. TiO<sub>2</sub> is a chemically stable compound, very common, non-expensive and non-toxic. Schematic presentation of UV irradiation ( $\lambda < 380$  nm) of TiO<sub>2</sub> that promotes an electron from the valence band to the conduction band (band gap energy 3.2 eV) leaving a positive hole behind is illustrated in Fig. 1.

In this process TiO<sub>2</sub> particles behave like electron donors or acceptors for molecules reaching the surface of the semiconductor. Positive holes and electrons as very active species participate in redox reactions on the surface of the semiconductor with water, oxygen, adsorbed organic or inorganic compounds leading to the mineralization of the pollutants. Positive holes and electrons can

also react directly with adsorbed organic or inorganic compounds on the semiconductor surface. However due to the fact that water molecules and oxygen are more abundant than contaminant molecules under normal conditions, basic processes on the semiconductor surface are guided by the reaction of h<sup>+</sup> and e<sup>−</sup> with water molecules and oxygen leading to the formation as intermediates of very powerful radicals like hydroxyl (OH•) – and superoxide radicals (O<sub>2</sub>•<sup>−</sup>) radicals, which are considered responsible for the redox processes at the semiconductor surface promoting the total degradation of pollutants as illustrated in Fig. 1.

However, as noted earlier, positive holes and electrons may readily recombine. In this case no reaction is taking place. Therefore, a prime challenging task for an effective process is to inhibit recombination of charge carriers in order to maintain the activity of the photo-catalyst high. In this context, as stated above, mixed phases of anatase and rutile, the dominant crystal structures of TiO<sub>2</sub>, may strongly promote charge separation through trapping of holes and electrons across the different crystal phases [22]. Charge separation of photo-generated species can also be achieved through doping of TiO<sub>2</sub> with metals and non-metals, which are introduced into the crystal lattice of TiO<sub>2</sub> without changing its basic crystallographic form. In addition, doping of semiconductors generally leads to a more efficient use of the solar spectrum radiation, considering that the UV part makes 5–8% of the solar spectrum only, while the visible part accounts for more than 43%, enabling the activation of the semiconductors e.g. TiO<sub>2</sub> at longer wavelengths (red shift,  $\lambda > 380$  nm). For instance in the case of manganese (Mn) the doping processes taking place, are presented in Fig. 2. Mn<sup>2+</sup> has valence electronic configuration of 3d<sup>5</sup>. When it traps electrons with Mn<sup>2+</sup> the electronic configuration changes to d<sup>6</sup> (Mn<sup>+</sup>) and if it traps with holes the electronic configuration changes to d<sup>4</sup> (Mn<sup>3+</sup>), both unstable, as shown in reactions (1–4).

Concerted efforts are on the way to further improve existing or even prepare new materials, which can be used under solar or visible light irradiation for the transformation/degradation of environmental pollutants/contaminants in indoor and outdoor environments. In this context, apart from the development of new dopant photo-catalysts, additional support materials are needed to increase the surface area and provide additional stability to the photo-catalyst.

In the past, photo-induced reactions in the heterogeneous phase e.g. on silica gel leading to the degradation of organic priority pollutants have been extensively studied [18,23]. With the use of semiconductor oxides as photo-catalysts the area of heterogeneous

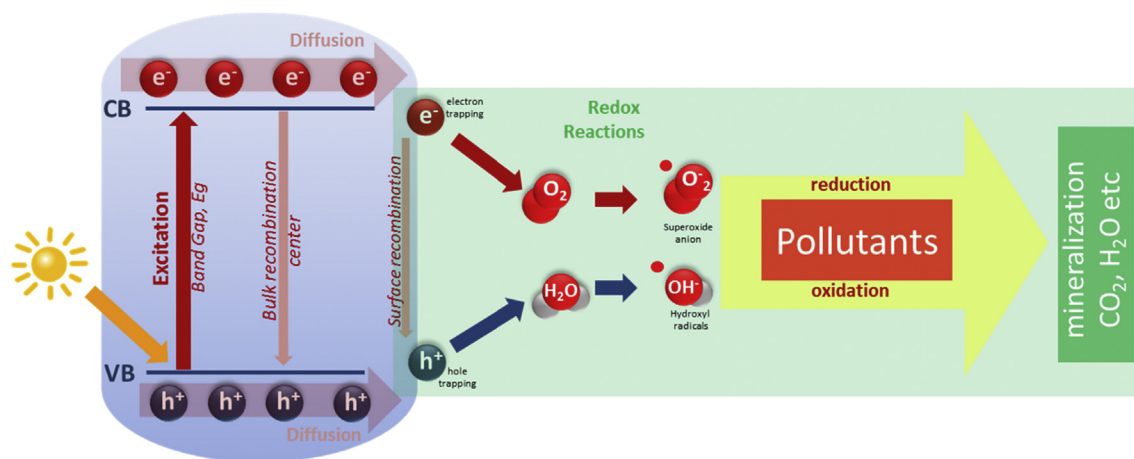


Fig. 1. Primary processes in semiconductor photocatalysis.

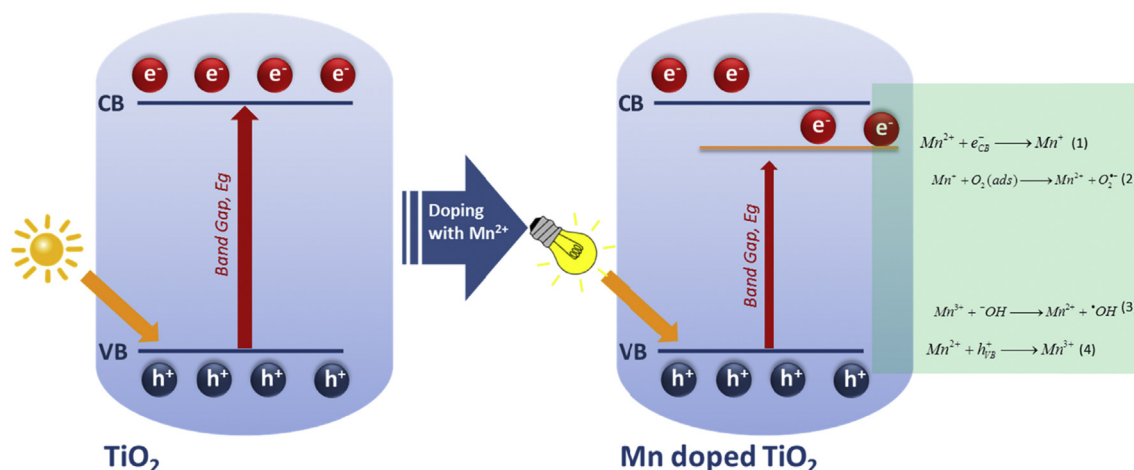


Fig. 2. Charge – carrier distribution of manganese (Mn) doped TiO<sub>2</sub>.

photo-catalysis has expanded rapidly within the last decades, in particular regarding the application of photocatalytic building and construction materials. TiO<sub>2</sub> due to its unique chemical characteristics has attracted the interest of researchers from academia and industry and has also become one of the most used photo-catalyst worldwide for the development of innovative building envelope material coatings capable to degrade inorganic and organic pollutants. Since un-doped TiO<sub>2</sub> can only be activated by UV light, there is a need to develop modified TiO<sub>2</sub> based photo-catalysts i.e. by doping that can induce its activation under visible light. This way, its application range may be extended to cover indoor environments too. One way of doing this is doping.

## 2.2. Electronic, structural and physicochemical studies on titania (TiO<sub>2</sub>)

The physicochemical properties of TiO<sub>2</sub> and the effect on its applications depend on parameters such as crystalline structure, particle size, preparation method, surface area and morphology, porosity and ratio of polymorphs. Regarding structure, TiO<sub>2</sub>, as mentioned above, is known to be forming three crystalline polymorphs, i.e. anatase, rutile and brookite, of which anatase and rutile are tetragonal. In this structure, each octahedron is sharing corners to form (001) planes for anatase and edge sharing octahedrons forming (001) planes for rutile [24] as illustrated in Fig. 3. On the other hand the orthorhombic structure of brookite phase is made up of both corner and an edge sharing octahedral. Anatase and rutile are meta-stable phases with the brookite being the most thermodynamic stable one. Due to these different crystal structures their subsequent density and electronic structures are different leading to diverse photo-catalytic activities and electronic responses. Although research on TiO<sub>2</sub> has focused on stabilizing the tetragonal-anatase phase of this oxide due to its excellent catalytic properties [25], mixture of anatase and rutile phase materials such as that of the industrial Degussa P-25 (30% rutile – 70% anatase) have been proved particularly effective [22].

In all current applications, it is generally accepted that TiO<sub>2</sub> is slightly off-stoichiometric with a number of oxygen vacancies giving rise to its n-type behavior. Besides crystal structure and phase mixture, important parameter underlining the effectiveness of this metal oxide semiconductor as photo-catalytic material is its band gap, the value of which determines the range and volume of energy it may absorb, thus controlling the amount of electron–hole pairs produced. Using a wide band gap semiconductor as photo-catalyst in which electrons from the valence band are excited to

the conduction band thus resulting in the formation of electron–hole (e<sup>-</sup>–h<sup>+</sup>) pairs, one is restricted to the range of energies that surpass the corresponding band gap energy. In the case of anatase TiO<sub>2</sub>, accepted as the most photo-catalytically active polymorph due to its superior mobility of e<sup>-</sup>–h<sup>+</sup> pairs, this energy corresponds to wavelengths of <390 nm i.e. the harmful UV radiation which is a small fraction of the solar radiation as suitable for the excitation process, thus restricting the range of photo-catalytic to outdoor applications only. However, effective band gap engineering utilizing semiconductor doping techniques may lead to band gap narrowing allowing the initiation of the activation process by photons of smaller energy thus utilizing part of the visible part of the solar spectrum too.

Successful efforts on doping either by non-metal or metal ions have opened up the field of indoor depollution utilizing visible light photo-catalysts. Nevertheless, besides the crystal structure and polymorph ratio, the issue of effectiveness either of undoped or doped TiO<sub>2</sub> is underpinned by the so called e<sup>-</sup> – h<sup>+</sup> pair recombination ratio i.e. the time span that the generated electrons and holes remain available for reacting with surrounding surface adsorbed H<sub>2</sub>O molecules to form, among other, hydroxyl and super oxide radicals. It is reported that in doped TiO<sub>2</sub> materials the dopants can induce shallow donor or acceptor states and lead to prolonged carrier diffusion lengths, thus facilitate recombination inhibition resulting to enhanced photo-catalytic activity. However, this may not be taken as a general rule as, in numerous cases, the presence of dopants, despite the achieved red shift in optical absorption edges as the result of the dopant presence, induce defect states which themselves act as carrier recombination centers on migrating carriers from the inside of the photo-catalyst to the surface [26,27]. As mentioned above, mixture of TiO<sub>2</sub> polymorphs has also been reported of their ability to inhibit the electron-hole recombination rate too while charge separation is another key factor addressed lately particularly for visible-light water splitting and water purification [28].

In as far as visible light photo-catalysts are concerned, as analyzed above the major drawback for pure TiO<sub>2</sub> is its large band gap and the solution to obtain a photocatalytic activity in the visible region is to modify the semiconductor either by doping the oxide with non-metal, transition metals and other metal oxides such as WO<sub>3</sub> or by dye-sensitization [29]. There are also studies that support the idea that one of the ways to improve the photocatalytic performance is by increasing the number and strength of acid sites in the catalysts [30]. Although dye-sensitization is a widely used technique particularly in photovoltaic systems in the absence of



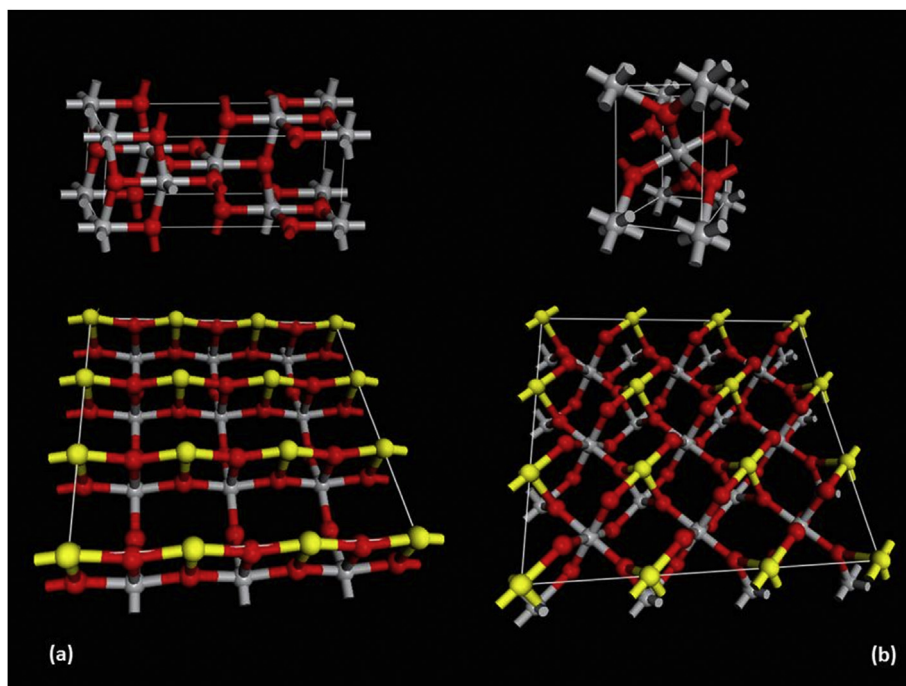


Fig. 3. Crystalline structures of anatase (a) and rutile (b), the yellow spheres are titanium atoms on the surface layer.

semiconductor charge separators, the photocatalytic efficiency of these dyes is rather poor. On the contrary, doping with noble metals such as Pt, Pd, Ag, Au etc has been proved very effective for visible-light activation due to the effective transfer of the photo-generated electrons from the conduction band of  $\text{TiO}_2$  to the metal particles induced by their lower Fermi levels with respect to that of  $\text{TiO}_2$ . Superior visible-light photocatalytic activity has been reported from transition metal doping and in particular Fe, Cu [31,32] and recently for Mn [33,34]. In 2003, the group of Kisch [35] first reported visible-light photo-catalysis utilizing carbon-doped  $\text{TiO}_2$  and attributed its activation to the formation of  $\text{Ti}^{3+}$  and oxygen vacancies due to the presence of carbon. Successful doping attempts regard the application of Sulfur, Fluorine, Iodine, Selenium and Boron followed right after [36–39]. Recently, graphene- $\text{TiO}_2$  composites have emerged with excellent photocatalytic activity synthesized by chemical and hydrothermal reduction as a suspension or as thin films of graphene oxides (RGO) [40].

In most material combinations, controlling the structure and morphology properties is essential for the degree of material activity [41]. There are numerous reports on a number of diverse synthetic methods leading to the formation of titanium oxide acquiring the tetragonal-anatase structure with enhanced photocatalytic activity. Among these physical and chemical techniques one may note the most important such as sputtering, pulsed laser deposition (PLD), sol–gel, hydrolysis of inorganic salts, and some hydrothermal processes for, among other,  $\text{TiO}_2$ -Graphene Oxide ( $\text{TiO}_2$  – GO) nanocomposite development [42]. Now-a-days, the sol–gel method and hydrothermal process are the most common inexpensive synthetic routes used to synthesize most transition metal oxide previously mentioned.

### 3. Strategies for improving titania photoactivity with transition metal doping for visible light applications

It has been underlined that the fundamental principle of photocatalysis is the ability of a photo-catalyst to absorb photons creating very active species which are capable to participate in redox

reactions of most organic and inorganic compounds leading to the mineralization of the pollutants. In line with other photo-catalysts, the activity of  $\text{TiO}_2$  depends on the lifetime of charge carriers generated on the surface. Surface electron – holes recombination is extremely high with most of charge carriers recombining on the surface before the redox reactions and this recombination rate must be reduced in order to improve the photocatalytic activity. As stated above, one way to reduce it is by doping with transition metal cations, which create traps for electrons and/or holes that subsequently immobilize the charge carriers and thus reduce the recombination rate. On the other hand doping induces a bathochromic shift i.e. a decrease of the band gap with the introduction of intra band gap states which lead to an enhanced absorption in the visible light region. Several transition metals such as V, Cr, Fe, Mn, Ni, Co, Cu, Zn [43–52] have been investigated previously in the attempt to create a shift of the energy band gap and to extend the spectral response of modified  $\text{TiO}_2$  towards the visible light region. The red shift of the absorption edge into the visible region can be assigned to the charge transfer between the d electrons of the transition metals (dopant) and the conduction (or the valance) band and appears to be a complex function of the dopant concentration, the energy level of the dopants, their electronic configuration and the applied light intensity.

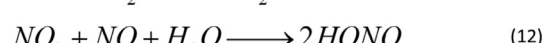
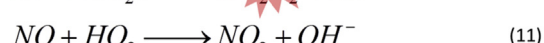
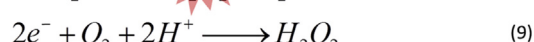
Key parameters that influence the photocatalytic degradation of pollutants under visible light irradiation are the type of the dopant (transition metal, oxidation states, size), the concentration and the microstructural and morphological characteristics of the modified  $\text{TiO}_2$ . Choi et al. performed a systematic study of  $\text{TiO}_2$  nanoparticles doped with 21 metal ions and found that the presence of metal ion dopants significantly influences the activity and its charge carrier recombination rates [31]. Devi et al reported in a review article that, if the dopant having higher ionic size (like  $\text{Mn}^{2+}$ ,  $\text{Zr}^{4+}$ ) substitutes the  $\text{Ti}^{4+}$  ion in the  $\text{TiO}_2$  lattice this leads to structural defects such as vacancies, particularly on the surface and thus more oxygen may escape from the lattice to trap the photo-generated holes and form hydroxyl radicals, preventing electron-hole recombination [53]. Verykios et al reported that the doping with

higher valent cation compared to  $\text{Ti}^{4+}$  shows enhanced photocatalytic activity compared with lower valent cation [54]. Bechne-mann and Hoffmann described the development of visible light responsive photocatalysts by incorporating small amounts of components such as cations and metal oxide. Many studies have demonstrated that the concentration of dopant is critical and affects the photocatalytic activity. However, there is an optimum amount of doping concentration beyond which any further increase could enhance the recombination rate of charge carriers, thus decrease the photocatalytic activity. Binas et al. demonstrated that for the case of Mn– $\text{TiO}_2$  doping, such an optimum ratio is at 0.1% (w/w) with ~20 nm particle size. In their report, the effect of Mn-doped  $\text{TiO}_2$  as a function of Mn concentration and the corresponding shift of the absorption edge was studied and subsequently contrasted with the resulting photocatalytic activity. At first, the introduction of small amounts of  $\text{Mn}^{2+}$  into  $\text{TiO}_2$  leads to a significant shift of the absorption edge towards the visible range (about 20 nm) as compared with commercial (P25)  $\text{TiO}_2$  showing a single intense absorption edge around 400 nm due to a charge transfer transition between the lattice oxygen ligands ( $\text{O}_2^-$ ) and a titanium ion ( $\text{Ti}^{4+}$ ). Further increase of the Mn dopant concentration up to 1% leads to a gradual increase in the sub-bandgap absorption with no apparent further red shift. In the case of Mn doped  $\text{TiO}_2$ , the corresponding red shift in the band gap transition (Fig. 4) and the resulting visible light absorption has been attributed to a charge transfer between the Mn dopant (d electrons) and CB (or VB) i.e. a d-d transition in the crystal field as described by Hoffman [31].

#### 4. Applications of modified $\text{TiO}_2$ for improved air and health quality

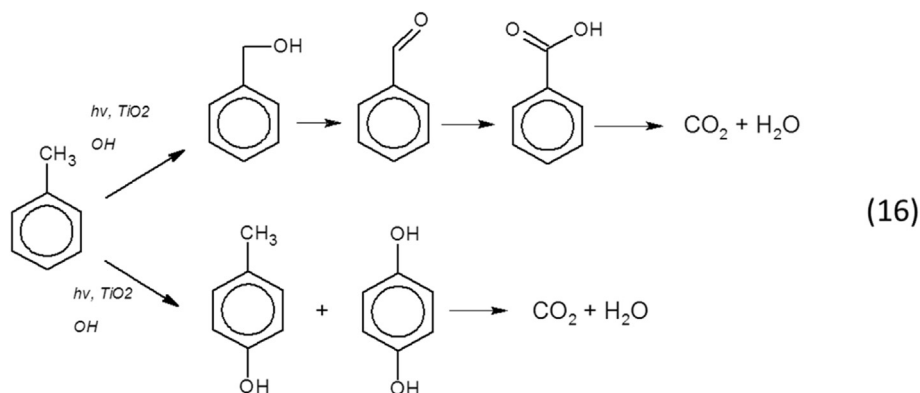
##### 4.1. Air quality

Laboratory and real scale data obtained by researchers within the framework of various projects indicated that, upon irradiation with UV light,  $\text{TiO}_2$  containing paints efficiently destroy the ozone precursors NO and  $\text{NO}_2$  up to 80% and 30%, respectively. The photocatalytic conversion of NO was found to increase with the decrease of relative humidity (50%→20%) and the photocatalytic rate of NO was calculated to be between  $0.11 \mu\text{g m}^{-2}\text{s}$  and  $0.42 \mu\text{g m}^{-2}\text{s}$ , depending on the humidity level [17,55]. The basic processes taking place at the air/semiconductor interface in the presence of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , NO and  $\text{NO}_2$  leading to the formation of nitrates and nitrites are as follows:



Apart from  $\text{NO}_x$ , chamber experiments done with various photo-catalytic paints for the removal of organic compounds e.g. toluene indicated a varying degradation of toluene between 8% and 90%, depending of the photo-catalytic material used. Degradation of toluene was affected by the relative humidity, as in the case of the degradation of NO, too [10]. Volatile organic compounds such as toluene and benzene, which are belonging to priority air pollutants in outdoor and indoor environments, were also tested within an EU research project (Clear-up/Resource efficient buildings for real life [20]), as individual compounds and as mixtures to evaluate their removal over  $\text{TiO}_2$  containing mineral silicate paints irradiated with UV light. The results were very promising and indicated that  $\text{TiO}_2$  containing coatings substantially degrade these compounds either as individual compounds or as mixtures. After 7 h of irradiation toluene was degraded to almost 90% (RH 20%), while degradation of toluene in a mixture with NO or benzene was faster, up to 90%, after 4 h only. Repeating these experiments by changing the relative humidity (RH) from 20% to 60% the conversion of toluene either as individual compound or as a mixture with NO and benzene was found to be much slower (up to 75%) as shown in Fig. 5.

A schematic presentation of the involved reactions during the photocatalytic degradation of Toluene is given below:



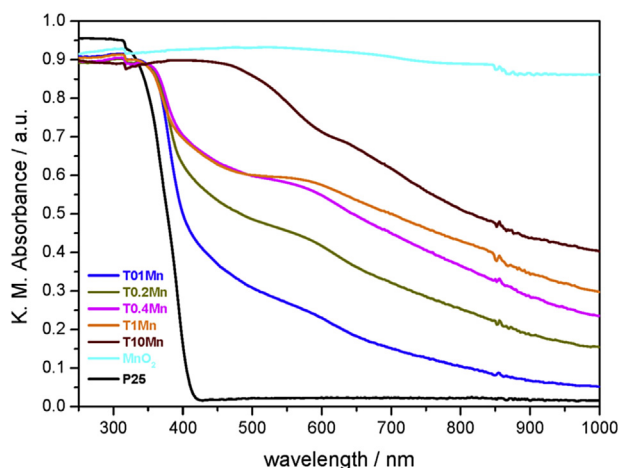


Fig. 4. UV-Vis absorption Spectra (diffuse reflectance) of P25, and 0.1, 0.2, 0.4, 1 and 10% Mn doped  $\text{TiO}_2$ .

The OH radical formation appearing during the irradiation of  $\text{TiO}_2$  was calculated on the basis of their reaction with toluene. Although the calculation of the formed OH radicals at 20% relative humidity of the order of  $1.6 \times 10^7$  and  $6.2 \times 10^6$  molecules/ $\text{cm}^3$  at

60% needs to be confirmed, it nevertheless shows an almost one order of magnitude difference in the formation of OH radicals by the irradiation of  $\text{TiO}_2$  at various humidity levels.

The effectiveness and ultimately the usability of the above optimized Mn-doped  $\text{TiO}_2$  materials on air-quality control applications was demonstrated by their incorporation into a calcareous matrix commonly used as a constituent of building products. Results have shown that Mn-doped  $\text{TiO}_2$  photo-catalyst upon irradiation with visible light may degrade up to 95% of NO after 6 h of irradiation, without any significant photo-catalyst inactivation. It should be noted that the most effective degradation rate was obtained for the 0.1% Mn-doping photo-catalytic coatings under visible light irradiation (Fig. 6). Incorporation of this optimum doping rate into a calcareous filler matrix at total volume concentrations of 5% and 10%, under that same illumination conditions the rate of NO degradation was higher on the filler panel surfaces with twice as much photocatalytic (0.1% Mn– $\text{TiO}_2$ ) material (Fig. 7)

Photocatalytic activities of  $\text{TiO}_2$  and Mn doped  $\text{TiO}_2$  have also been investigated, besides the decomposition of NO, for acetaldehyde too in gas phase.

It was found that under visible light irradiation 0.1 Mn doped  $\text{TiO}_2$  shows high photocatalytic activity for the removal of acetaldehyde as compared to undoped and Mn doped with higher concentrations (Fig. 8). The end products analysis has shown that  $\text{CO}_2$  is the major photocatalytic product in acetaldehyde degradation

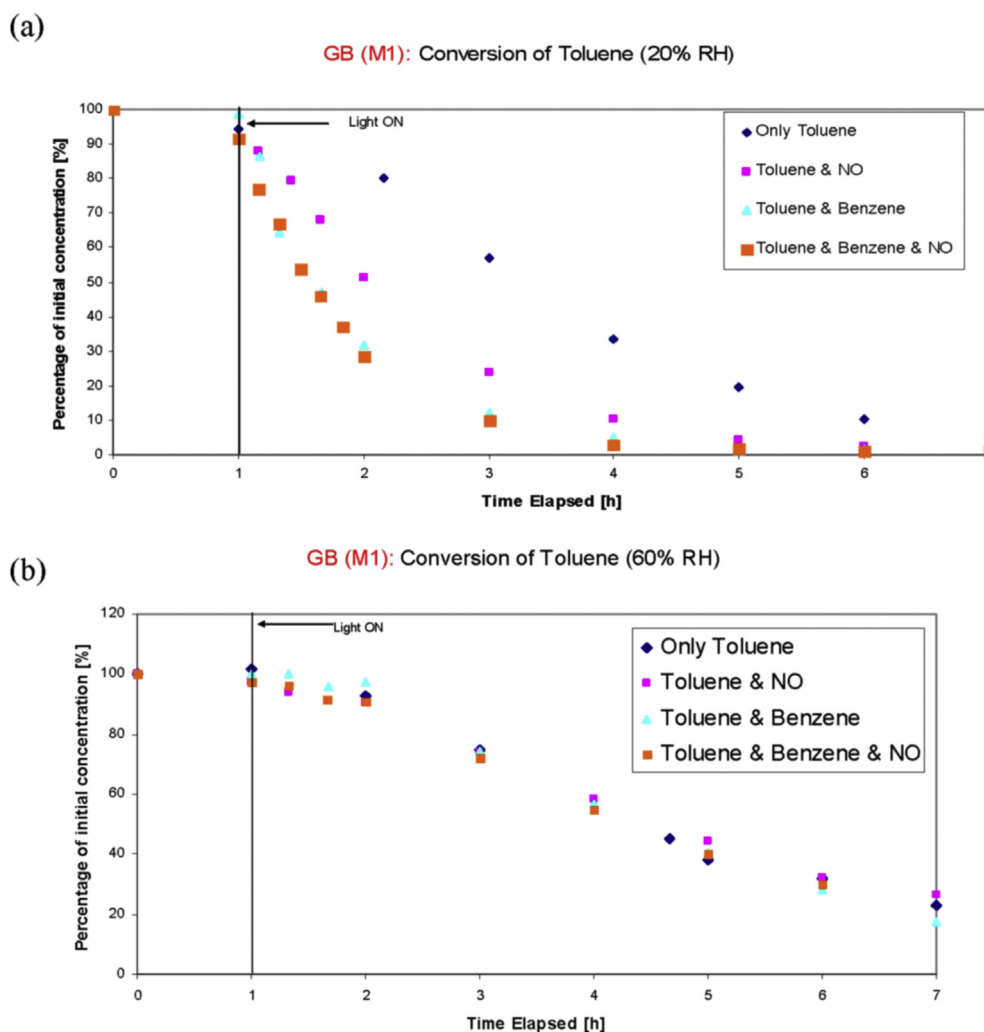


Fig. 5. Photocatalytic rate of toluene conversion affected both by RH and mixture (a, b).

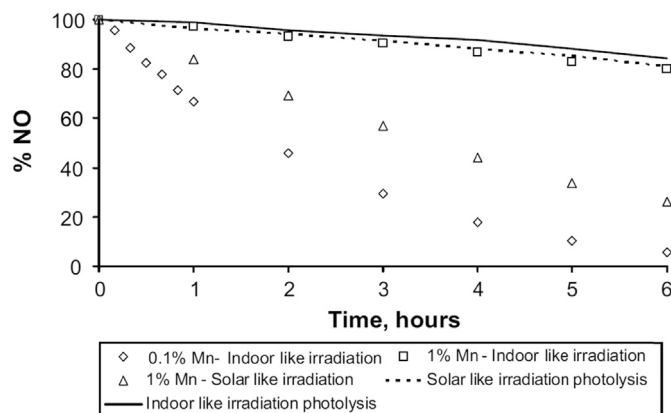


Fig. 6. Comparison of photolytic and photocatalytic decomposition of NO with Mn doped  $\text{TiO}_2$  catalysts containing 0.1 and 1% Mn under indoor- and solar-like illumination.

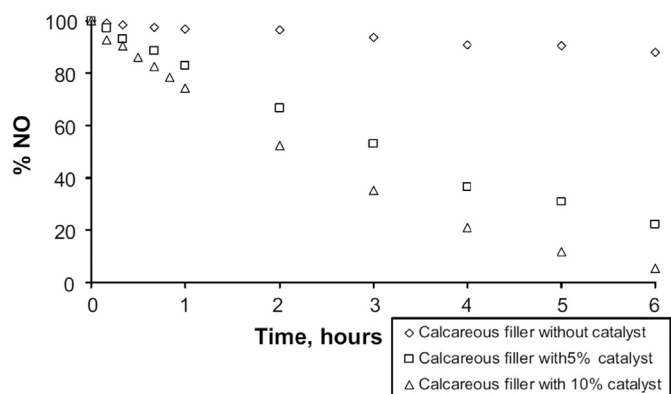


Fig. 7. Photocatalytic decomposition of NO by calcareous filler panels containing 0.1 Mn  $\text{TiO}_2$  photocatalyst.

with higher  $\text{CO}_2$  yields under UV light irradiation in comparison with visible light [56].

However, besides calcareous matrices the investigation has been extended by the introduction of Mn doped  $\text{TiO}_2$  into cementitious matrixes contain 5 and 10% of the photocatalytic material under UV visible light irradiation. Kotzias et al. have studied the photocatalytic activity of smart photocatalytic paints and showed that when added to a building material matrix (inorganic paint) the photo-catalyst (0.1% Mn doped  $\text{TiO}_2$ ) still remains active for the degradation of NO. Following a 6 h exposure under visible light, NO was degraded efficiently in the presence of panels containing 5 and 10% of the 0.1% Mn doped  $\text{TiO}_2$  photo-catalyst by up to 80 and 95% respectively (Fig. 9).

The useful message obtained as an outcome of these experiments was that, upon selection of both, appropriate dopant type and its concentration in the crystal lattice of  $\text{TiO}_2$ , the photo-assisted elimination of air pollutants using semiconductor oxides

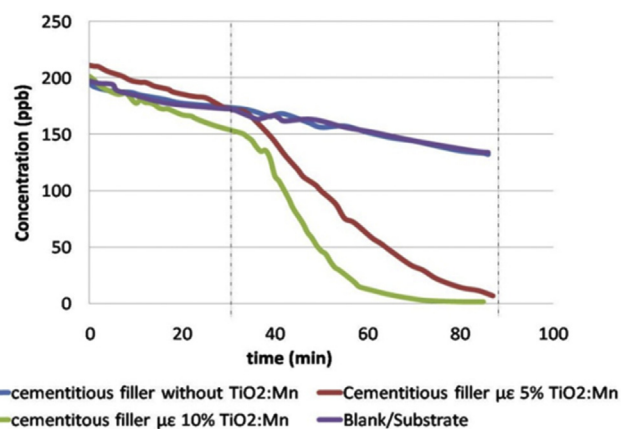


Fig. 9. Photocatalytic decomposition of NO by cementitious filler panels containing 0.1 Mn  $\text{TiO}_2$ .

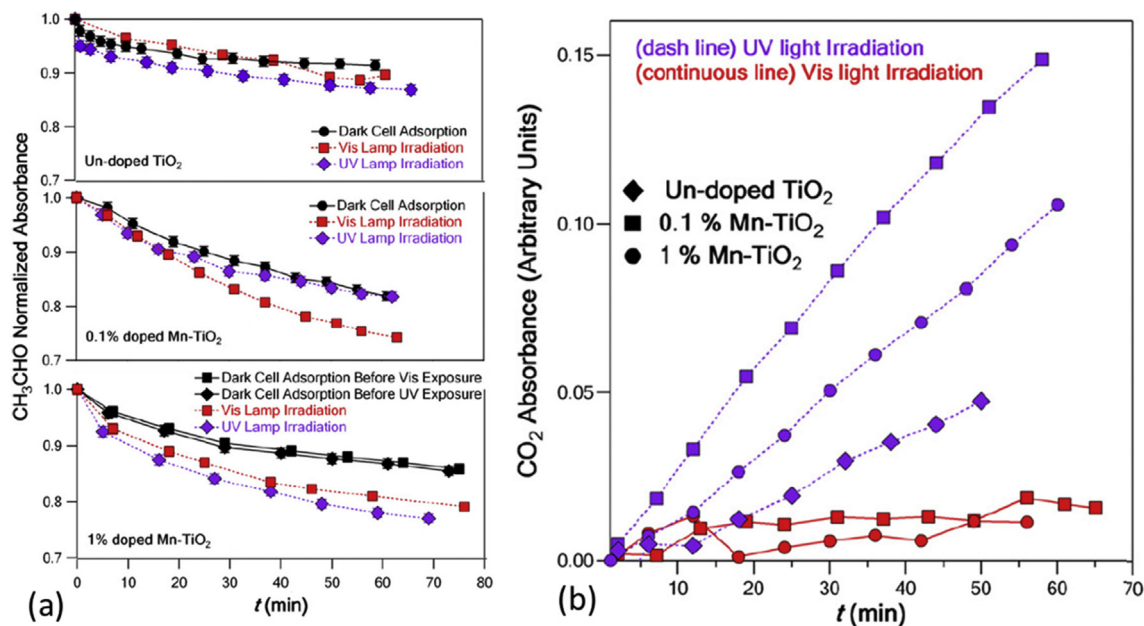


Fig. 8. Comparison of photocatalytic degradation of acetaldehyde with Mn doped  $\text{TiO}_2$  under UV and Visible irradiation (a) and  $\text{CO}_2$  formation during each process (b).



may be a promising technique for remediation purposes in indoor environments.

In all de-pollution processes, choosing the right photo-catalyst with the highest activity and durability is only the one side of the problem. However, choosing the right matrices for the incorporation of the optimized photo-catalysts in such a way that the side effects of the photocatalytic process either under UV or visible light exposure is of paramount importance too. Indeed one should be very careful of the type and concentration of by-product formation which may render a photocatalytic commercial product from lunched in the market. This is particularly important for photo-catalytic paints due to the numerous types commercially available containing an endless list of organic and inorganic substances serving the consumers' needs.

Assessing the de-polluting efficiency of photo-catalytically active paints, one may observe the formation of carbonyls while irradiating with UV light. This observation is confirmed by a number of studies conducted in the past. Long term UV irradiation experiments with a photo-catalytic paint of known composition for a period of 14 days showed the formation of low molecular weight carbonyls [57]. The formation of carbonyls decreases in the course of the irradiation. In addition, components of the paint were irradiated separately in the presence/absence of titanium dioxide as reference. Formaldehyde, acetaldehyde, propanol and acetone (in decreasing order of concentration) were the main carbonyls identified.

In this context, within the framework of our investigations, evaluating the depollution efficiency for priority air pollutants by photocatalytic coatings e.g. paints we did study the type and contents of by-products formation. In this practice, we often observed the formation of low molecular weight carbonyl compounds e.g. formaldehyde, acetaldehyde as by-products following irradiations with UV light. By-products can be formed either as intermediate products from the incomplete photo-catalysis of pollutants or as secondary products due to degradation of supporting materials (components) in the coatings, which basically serve to increase the stability and consistency of coatings. Supporting materials are resins, cohesion agents, super plasticizers and defoamers; mostly

organic polymers, organic dyes, aliphatic and aromatic solvents. Degradation of these components while irradiating the  $\text{TiO}_2$  based coatings leads to increased formation of aldehydes and ketones as by-products (Fig. 10). This has been demonstrated by the irradiation of the individual components in the presence of  $\text{TiO}_2$ .

Organic polymers as paint constituents were found to be the main source for the formation of the carbonyls [58,59]. A possible solution to avoid or diminish the formation of by-products when using semiconductor based coatings may be the development of more stable paint components. Another possibility to avoid/minimize secondary emissions would be the pre-treatment of the photocatalytic coating prior to commercial distribution over a longer period of time. Recent studies indicated that secondary emissions of carbonyl compounds are considered negligible after irradiation of the coatings over a period of three weeks.

In conclusion, it should be underlined that the development of innovative building materials and coatings (containing  $\text{TiO}_2$ ) and, in particular, the development of modified catalysts activated by visible light are two fields of innovative research that will keep been active for years to come. Moreover, targeted studies are needed addressing the efficiency of photocatalytic materials on the degradation of chemical mixtures including the determination of eventually formed, toxicologically relevant, by-products in an effort to evaluate the applicability of these materials as indoor coatings on a number of surfaces thus improving indoor/outdoor air quality. In this context, the combined disinfecting properties of these photo-catalysts are promoted and as such are analyzed in the following.

#### 4.2. Disinfection

The increased human exposure to microbial pathogens has always been an issue of general interest, as it may lead to the emergence and dissemination of diseases with considerable socio-economic impacts. Bioaerosols, which are suspensions of airborne pathogens, or are released from living organisms, contribute in indoor air pollution. Bacteria, fungi and viruses are enlisted among them, causing serious diseases and contributing in the transmission of tuberculosis, influenza, pneumonia and many others [2,60]. The

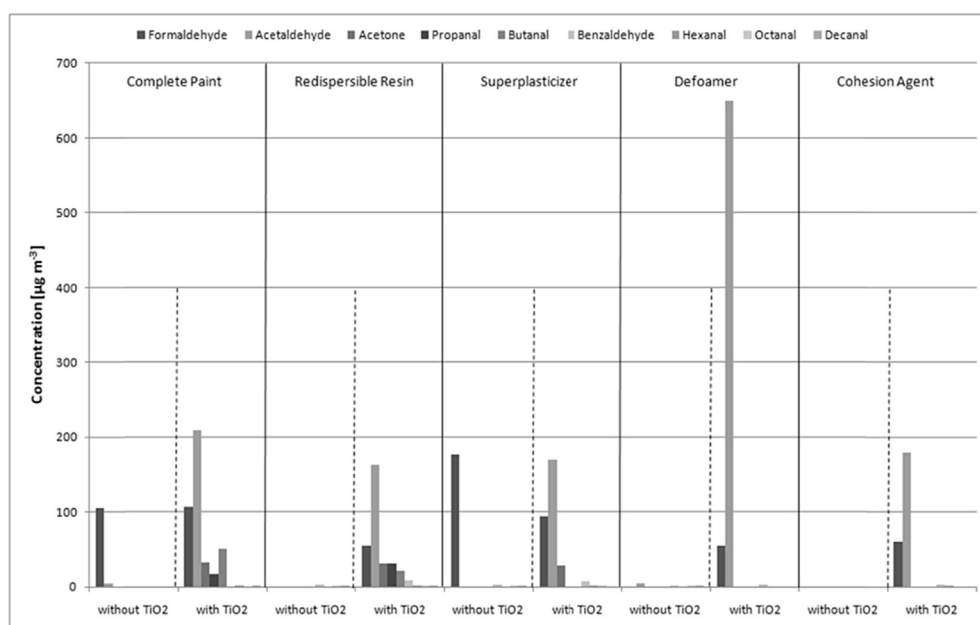


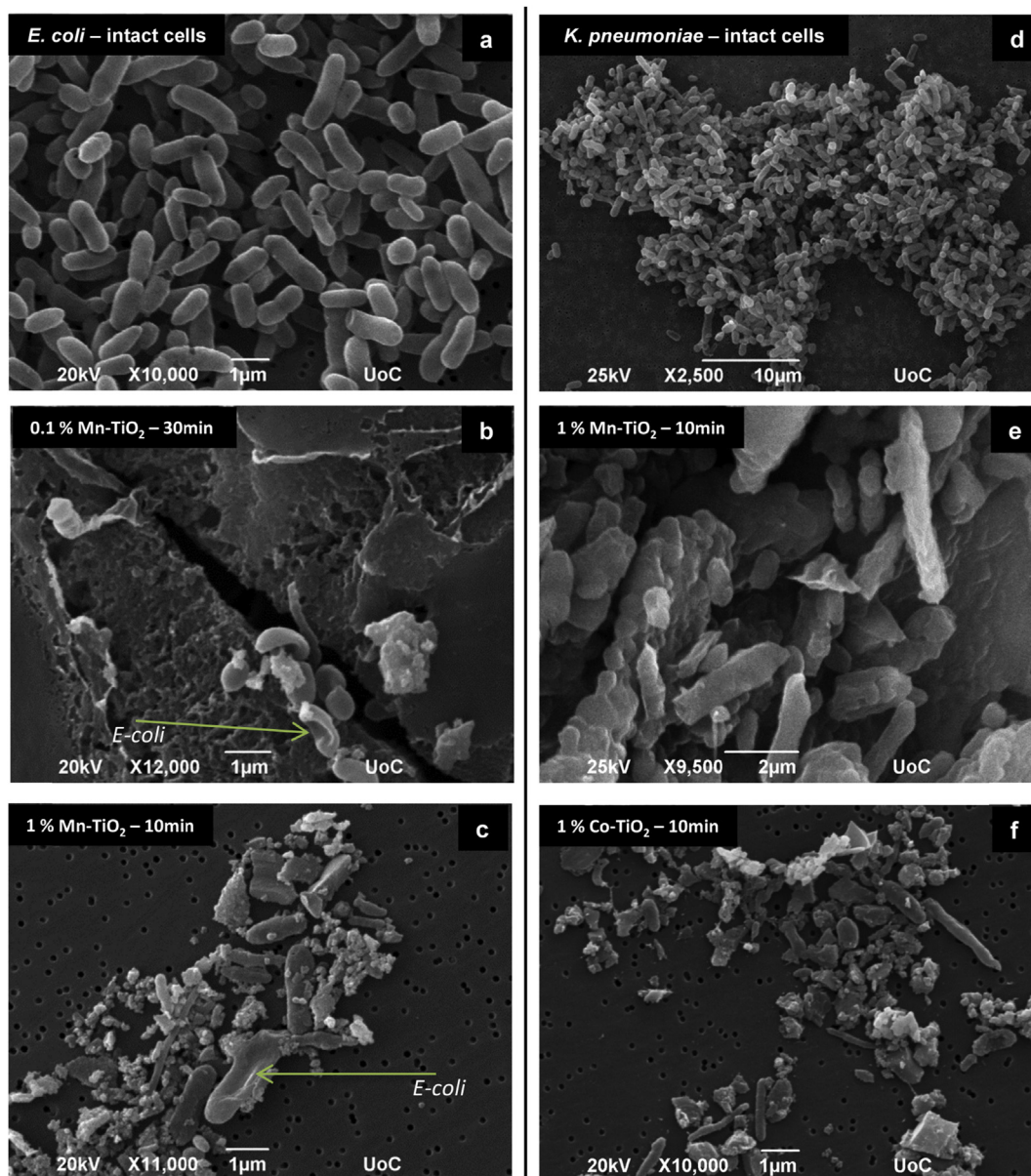
Fig. 10. Formation of carbonyls whilst irradiating single components of the paint in the presence/absence of  $\text{TiO}_2$ .

ongoing research regarding disinfection explores different techniques, whose ultimate goal is the control of such disease-causing microorganisms to tolerable and acceptable limits for public health protection [3,61]. Disinfection is mostly referred to the inactivation of pathogenic and virulent microorganisms, without necessarily killing them. AOPs and  $\text{TiO}_2$ -based photo-catalysts have gained enormous attention during the past few decades as disinfection agents against various microorganisms, including the most persistent in the environment like viruses, bacterial spores and protozoan cysts. Their high oxidation potential results to the in situ generation of highly reactive transitory species, which ultimately “attack” microorganisms, inducing stressful conditions [15].

The response of microorganisms during photocatalysis is strongly affected by the cellular structure, components and forms, which vary extremely within the microbial world. Although many studies have already elucidated the general mechanisms of microbial inactivation, the detailed procedure concerning certain

groups is still in an early stage. The biocidal effect of photocatalysis is attributed to the generation of ROS, with hydroxyl radical ( $\text{HO}^\bullet$ ) followed by superoxide radical ( $\text{O}_2^{\bullet-}$ ), hydro-peroxyl radical ( $\text{HO}_2^\bullet$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) being the primary species responsible for microbial destruction [62]. The first step is the interaction between the microorganism and the nanoparticles of the catalyst affecting the outer cell wall components, followed by lesions in the cytoplasmic membrane (Fig. 11). The latter increase cell permeability, permitting the release of intracellular components into the external environment and inducing loss of viability [63]. Moreover, it has also been reported that cell death is achieved by the oxidation/reduction of the intracellular Coenzyme A (CoA), which inhibits the process of respiration [64].

The resistance level of bacteria varies among different groups and is affected by the thickness of the cell wall and the overall cellular form. According to many studies the order sensitivity for some bacteria is the following: Gram-negative bacteria (other than

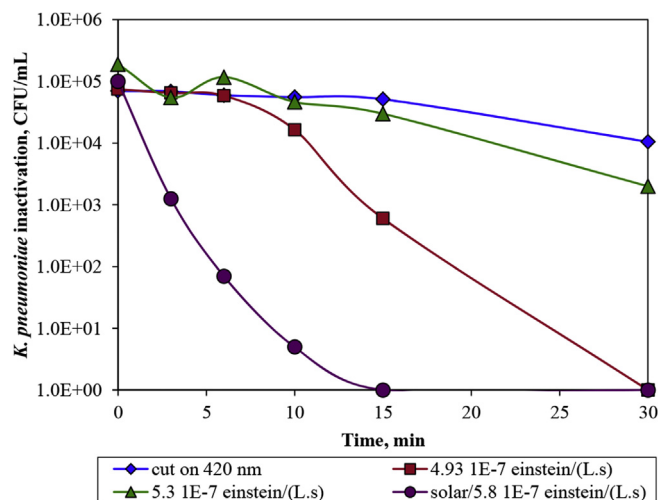


**Fig. 11.** SEM images of *E. coli* (a–c) and *K. pneumoniae* (d–f) without treatment (negative controls) and after photocatalytic treatment (simulated solar irradiation) in the presence of metal-doped  $\text{TiO}_2$ .

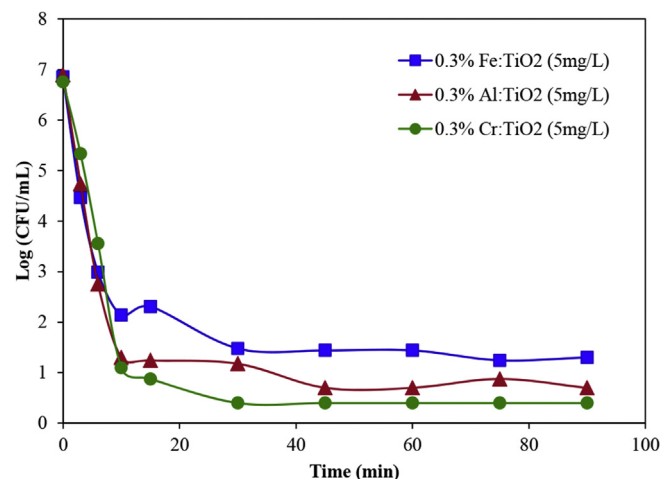
coliforms) > coliforms > *Enterococcus* sp. > other Gram-positive bacteria [11]. Gram positive species possess a thick cell wall with many layers of peptidoglycan and teichoic acids, which provides protection up to a certain extent as it obstructs penetration of free radicals [65]. Nevertheless, this precedence order may be reversed depending on the operational conditions and the bacterial indicators employed in each case. Yet, bacterial inactivation through photo-catalysis shows promise for widespread applications. Many different bacterial species show high inactivation rates on TiO<sub>2</sub> coated surface in air, making photo-catalysis a sufficient technique for the purification of indoor environment [60]. Further studies under visible light with doped titania materials (e.g. Ag–TiO<sub>2</sub>/GF), broaden the use of this technique, especially when UV irradiation is prohibited [2].

Venieri et al. have been studying solar photocatalysis for water/wastewater disinfection, employing various modified titania catalysts (e.g. Mn-, Co- and Mn/Co-binary doped titania) for the inactivation of *E. coli*, *Klebsiella pneumoniae* and coliphage MS2 [66–68]. Some representative results are shown in Fig. 12, where it is observed that *K. pneumoniae* may be inactivated satisfactory in aqueous matrix during solar photocatalysis with 1 wt% Mn-doped TiO<sub>2</sub>. Although the contribution of UV light was obvious, total removal of the bacterium occurred under simulated solar light at  $5.8 \times 10^{-7}$  E/(L.s), while longer periods were required at lower photon fluxes. Further satisfactory results were obtained when *Staphylococcus aureus* was the bacterium of our interest. Fe-, Al- and Cr-doped titania achieved an almost 7 Log reduction of the bacterial population within 30 min of exposure under simulated solar irradiation (Fig. 13).

Another group of microorganisms of great importance for the air quality of indoor environment includes fungi (filamentous forms and yeasts). Although research regarding fungi inactivation through photo-catalysis is quite limited the general observation is that they exhibit considerable tolerance, possibly due to the presence of chitin in their cell walls [64,69]. Rodrigues-Silva et al. [14], who performed gas-phase inactivation studies with different microorganisms, recorded the faster bacterial decay compared with the fungal one. Similarly, Pigeot-Rémy et al. [70], who tested the inactivation of *A. niger* spores from indoor air by photocatalytic filters, observed that long durations of exposure to UV-A or UV-C radiation were required for adequate fungal elimination.



**Fig. 12.** Inactivation of *Klebsiella pneumoniae* in water in the presence of 1 wt% Mn-doped TiO<sub>2</sub>. Runs were performed under simulated solar irradiation [irradiance:  $5.8 \times 10^{-7}$  E/(L.s)], with a 420 nm cutoff filter to remove all the UV light and with filters to reduce irradiance to  $5.3 \times 10^{-7}$  E/(L.s) and  $4.93 \times 10^{-7}$  E/(L.s), respectively. Catalyst concentration: 250 mg/L.



**Fig. 13.** *Staphylococcus aureus* inactivation under simulated solar irradiation in the presence of Fe-, Al- and Cr-doped TiO<sub>2</sub> catalysts.

Viruses are also included in microbial organisms, despite the lack of enzymes and cellular structure. Their remarkable tolerance under stressed environmental conditions has drawn the attention of researchers, since they are extremely dangerous for public health [71]. The inactivation of viruses in photocatalysis is initiated by their adsorption onto the catalysts nanoparticles followed by the attack on the protein capsid and the binding sites of the viruses [72]. Conversely, other studies suggest that the inactivation behavior of viruses, including phages, is mediated by free hydroxyl radicals in the bulk phase and not by those bound on the catalyst surface [73]. Kozlova et al. [74], who studied the inactivation of aerosol deposited model pathogenic microorganisms over TiO<sub>2</sub> and Pt/TiO<sub>2</sub>, found that vaccinia virus and influenza A virus (H<sub>3</sub>N<sub>2</sub>) were inactivated up to 99.8% within 30 min irradiation of Pt/TiO<sub>2</sub>.

In photocatalytic processes the ultimate target of ROS is the microbial genetic material. The crucial damages in DNA molecules are attributed to the attack of superoxide radicals and hydroxyl radicals, produced at the surface of titania during a photocatalytic process, while RNAs exhibit higher sensitivity and less stability [75]. All these structural damages are subject to restoration and microbial reactivation may occur under specific circumstances, depending on the properties of each microorganism. Although the mechanism of repair is usually activated in certain bacterial species upon UV-C irradiation, it has also been documented after exposure to UV-A irradiation [76]. This issue raises certain concerns regarding the durability of photocatalytic disinfection. However, permanent elimination of pathogens and public health protection may be accomplished after selection of the appropriate technique and standardization of its operational parameters.

## 5. Conclusions

It has been demonstrated that the removal of NO<sub>x</sub> gases and VOCs at typical urban/indoor air levels by the use of photo-catalytic (TiO<sub>2</sub>-based) technology is feasible. Moreover, TiO<sub>2</sub>-based photocatalysts have gained enormous attention during the past few decades as disinfection agents against various microorganisms, including the most persistent in the environment like viruses, bacterial spores and protozoan cysts.

Humidity affects both the NO<sub>x</sub> and VOC photo-degradation. An increase in humidity inhibits photo-oxidation, due to the competition of water molecules with pollutant molecules for adsorption sites.



Photo-catalytic paints, especially, for indoor environments need (regarding the ingredients/paint components) to be optimized in order to reduce or eliminate the emission/formation of harmful by-products.

With selection of both the appropriate dopant (i.e. Mn) and its concentration in TiO<sub>2</sub> coatings, the photo-induced elimination using visible light of indoor air contaminants is a promising technique for remediation purposes in confined environments. Furthermore, application of TiO<sub>2</sub>-based photocatalytic coatings can contribute to energy saving due to the reduction of ventilation rates in buildings.

On the other hand, the synthesis of new solar-active and stable photocatalysts can boost the technology of disinfection processes, towards an extensive variety of disease-causing microorganisms. In a nutshell, solar processes may prevail over other techniques in the quest of efficient disinfection/decontamination treatment technologies, since they exploit a renewable energy source, avoiding operational costs and other limitations associated with artificial illumination.

## 6. Future trends in photocatalysis

- The global market for photocatalytic materials and photocatalysts will increase in the next years, in particular in the construction sector.
- Development of innovative building materials and coatings (containing TiO<sub>2</sub>), in particular, the development of modified catalysts activated by visible light are two fields of innovative research to be addressed in future investigations.
- Targeted studies are needed addressing the efficiency of photocatalytic materials on the degradation of chemical and biological contaminants including the determination of eventually formed, toxicologically relevant, by-products in order to evaluate the applicability of these materials and coatings in indoor environments too.
- The disinfection performance of those materials is very promising, even for the inactivation of severe pathogens contained in water and indoor air environments. What is further required is the standardization of photocatalytic techniques for the establishment of their performance limits in each case. The latter is a function of the type of microorganism under investigation, the stringent legislations and the overall public health awareness.
- Research on the topic will maximize the performance of photocatalysis, with the view to apply it on a routine basis and in large-scale applications.

## Acknowledgements

This work was carried out as part of European Funding programs under the FP7 Clear – up IP project no 211948 and FP7-Regpot-2012-2013-1 under grant agreement No 316165. The authors would like to acknowledge Dr. E. Klontza for Fig. 3.

## References

- [1] Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J, Gernjak W. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catal Today* 2009;147:1–59.
- [2] Pham TD, Lee BK. Feasibility of silver doped TiO<sub>2</sub>/glass fiber photocatalyst under visible irradiation as an indoor air germicide. *Int J Environ Res Public Health* 2014;11:3271–88.
- [3] Pepper IL, Gerba CP, Gentry TJ. *Environmental microbiology*. 3rd ed. Academic Press; 2015.
- [4] Janes H, Sheppard L, Shepherd K. Statistical analysis of air pollution panel studies: an illustration. In: UW biostatistics working paper series. Working paper 300; October 2006. <http://biostatistics.bepress.com/uwbiostat/paper300>.
- [5] Fisher MB, Keane DA, Fernández-Ibáñez P, Colreavy J, Hinder SJ, McGuigan KG, et al. Nitrogen and copper doped solar light active TiO<sub>2</sub> photocatalysts for water decontamination. *Appl Catal B Environ* 2013;130–131:8–13.
- [6] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. *Chem Rev* 1995;95:69–96.
- [7] Maira AJ, Yeung KL, Soria J, Coronado JM, Belver C, Lee CY, et al. Gas-phase photo-oxidation of toluene using nanometer-size TiO<sub>2</sub> catalysts. *Appl Catal B Environ* 2001;29:327–36.
- [8] Strini A, Cassese S, Schiavi L. Measurement of benzene, toluene, ethylbenzene and O-xylene gas phase photodegradation by titanium dioxides dispersed in cementitious materials using a mixed flow reactor. *Appl Catal B-Environ* 2005;61:90–7.
- [9] Agrios AG, Gray K, Weitz E. Photocatalytic transformation of 2,4,5-Trichlorophenol on TiO<sub>2</sub> under sub-band-gap illumination. *Langmuir* 2003;19:1402–9.
- [10] Maggos Th, Leva P, Bartzis JB, Vasilakos Ch, Kotzias D. Document gas phase photocatalytic oxidation of VOC using TiO<sub>2</sub> – containing paint: influence of NO and relative humidity, WIT. *Trans Ecol Environ* 2007;101:585–93.
- [11] Rodrigues-Silva C, Miranda SM, Lopes FVS, Silva M, Dezotti M, Silva AMT, et al. Bacteria and fungi inactivation by photocatalysis under UVA irradiation: liquid and gas phase. *Environ Sci Pollut Res* 2016;1–10.
- [12] Robertson PKJ, Robertson JMC, Bahnemann DW. Removal of microorganisms and their chemical metabolites from water using semiconductor photocatalysis. *J Hazard Mater* 2012;211–212:161–71.
- [13] Chuaybamroong P, Thunyasinron C, Supothina S, Sripenjalu P, Wu CY. Performance of photocatalytic lamps on reduction of culturable airborne microorganism concentration. *Chemosphere* 2011;83:730–5.
- [14] Pigeot-Rémy S, Lazzaroni JC, Simonet F, Pétiga P, Vallet P, et al. Guillard survival of bioaerosols in HVAC system photocatalytic filters. *Appl Catal B Environ* 2014;144:654–64.
- [15] Zhao Y, Aarnink AJA, Xin H. Inactivation of airborne *Enterococcus faecalis* and infectious bursal disease virus using a pilot-scale ultraviolet photocatalytic oxidation scrubber. *J Air Waste Manag Assoc* 2014;64:38–46.
- [16] Geiss O, Cacho C, Barrero-Moreno J, Kotzias D. Photocatalytic degradation of organic paint constituents-formation of carbonyls. *Build Environ* 2012;48:107–12.
- [17] Cacho C, Geiss O, Barrero-Moreno J, Binas VD, Kiriakidis G, Botallico L, et al. Studies on photo-induced NO removal by Mn-doped TiO<sub>2</sub> under indoor-like illumination conditions. *J Photochem Photobiol A Chem* 2011;222:304–6.
- [18] Sheehan P, Korte F, Bourdeau Ph, editors. Appraisal of tests to predict the environmental behaviour of chemicals. SCOPE by John Wiley&Sons; 1985. H. Parlar, D. Kotzias, Degradation in the Liquid and Adsorbed Phase, 81–105.
- [19] Fujishima A, Hashimoto K, Watanabe T. TiO<sub>2</sub> photocatalysis: fundamentals and applications. Japan: BKC Inc.; 1999.
- [20] Fujishima A, Zhang X, Tryk DA. TiO<sub>2</sub> photocatalysis and related surface phenomena. *Surf Sci Rep* 2008;63:515–82.
- [21] Daghrir R, Drogui P, Robert D. Modified TiO<sub>2</sub> for environmental photocatalytic applications: a review. *Ind Eng Chem Res* 2013;52:3581–99.
- [22] Ohtani B, Prieto-Mahaney O, Li D, Abe R. What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *J Photochem Photobiol A Chem* 2010;216:179–82.
- [23] Kotzias D, Klein W, Lotz F, Nitz S, Korte F. Photoinduced mineralization of organic chemicals. *Chemosphere* 1979;5:301–4.
- [24] Diebold U. The surface science of titanium dioxide. *Surf Sci Rep* 2003;48:53–229.
- [25] Nolan NT, Healy LF, Seery MK, Hinder SJ, Pillai SC. A systematic study of the effect of silver on the chelation of formic acid to a titanium precursor and the resulting effect on the anatase to rutile transformation of TiO<sub>2</sub>. *J Phys Chem C* 2010;114:13026–34.
- [26] Shao G. Red shift in manganese- and iron-doped TiO<sub>2</sub>: a DFT+U analysis. *J Phys Chem C* 2009;113:6800–8.
- [27] Li X, Chen X, Niu H, Han X, Zhang T, Liu J, et al. The synthesis of CdS/TiO<sub>2</sub> hetero-nanofibers with enhanced visible photocatalytic activity. *J Colloid Interface Sci* 2015;452:89–97.
- [28] Chen X, Shen S, Guo L, Mao SS. Semiconductor-based photocatalytic hydrogen generation. *Chem Rev* 2010;110:6503–70.
- [29] Cui Y, Du H, Wen L. Origin of visible-light-induced photocatalytic properties of S-doped anatase TiO<sub>2</sub> by first-principles investigation. *Solid State Commun* 2009;149:634–7.
- [30] Colón G, Hidalgo MC, Navio JA. Photocatalytic behaviour of sulphated TiO<sub>2</sub> for phenol degradation. *Appl Catal B Environ* 2003;45:39–50.
- [31] Choi W, Termin A, Hoffmann M. The role of metal ion dopants in quantum-sized TiO<sub>2</sub>: correlation between photoreactivity and charge carrier recombination dynamics. *J Phys Chem* 1994;84:13669–79.
- [32] Litter M. Heterogeneous photocatalysis: transition metal ions in photocatalytic systems. *Appl Catal B* 1999;23:89–114.
- [33] Wu X, Ma Z, Qin Y, Qi X, Liang Z, Chin J. *Chem Phys* 2004;20:138.
- [34] Binas VD, Sambani K, Maggos T, Katsanaki A, Kiriakidis G. Synthesis and photocatalytic activity of Mn-doped TiO<sub>2</sub> nanostructured powders under UV and visible light. *Appl Catal B Environ* 2012;113–114:79–86.
- [35] Sakthivel S, Kisch H. Daylight photocatalysis by carbon-modified titanium dioxide. *Angew Chem Int Ed Engl* 2003;42:4908–11.
- [36] Li D, Hamed H, Labhsetwar NK, Hishita S, Ohashi N. Visible-light-driven photocatalysis on fluorine-doped TiO<sub>2</sub> powders by the creation of surface oxygen vacancies. *Chem Phys Lett* 2005;401:579–84.
- [37] Liu G, Chen Z, Dong C, Zhao Y, Li F, Lu GQ, et al. Visible light photocatalyst: iodine-doped mesoporous titania with a bicrystalline framework. *J Phys Chem*



- B 2006;110:20823–8.
- [38] Chen D, Yang D, Wang Q, Jiang ZY. Effects of boron doping on photocatalytic activity and microstructure of titanium dioxide nanoparticles. *Ind Eng Chem Res* 2006;45:4110.
- [39] In S, Orlov A, Berg R, García F, Jimenez SP, Tikhov MS, et al. Effective visible light-activated B-doped and B,N-Codoped TiO<sub>2</sub> photocatalysts. *J Am Chem Soc* 2007;129:13790–1.
- [40] Tan LL, Ong WJ, Chai SP, Mohamed AR. Reduced graphene oxide-TiO<sub>2</sub> nanocomposite as a promising visible-light-active photocatalyst for the conversion of carbon dioxide. *Nanoscale Res Lett* 2013;8:465.
- [41] Addamo M, Augugliaro V, Di Paola A, García-López E, Loddo V, Marci G, et al. Preparation, characterization, and photoactivity of polycrystalline nanostructured TiO<sub>2</sub> catalysts. *J Phys Chem B* 2004;108:3303–10.
- [42] Stengl V, Bakardjieva S, Matys Grygar T, Bludská J, Kormunda M. TiO<sub>2</sub>-graphene oxide nanocomposite as advanced photocatalytic materials. *Chem Central J* 2013;7:41.
- [43] Yamashita H, Harada M, Misaka J, Takeuchi M, Ikeue K, Anpo M. Degradation of propanol diluted in water under visible light irradiation using metal ion implanted titanium dioxide photocatalysts. *J Photochem Photobiol A Chem* 2002;148:257–61.
- [44] Tsuyumoto I, Nawa K. Thermochromism of vanadium-titanium oxide prepared from peroxovanadate and peroxotitanate. *J Mater. Sci* 2008;43:985–8.
- [45] Wu S, Ma Z, Qin Y, Qi Z, Liang C. Photocatalytic redox activity of doped nanocrystalline TiO<sub>2</sub>. *Acta Phys-Chim Sin* 2004;20:138–43.
- [46] Mohamed M, Othman I, Mohamed M. Synthesis and characterization of MnO<sub>x</sub>/TiO<sub>2</sub> nanoparticles for photocatalytic oxidation of indigo carmine dye. *J Photochem Photobiol A* 2007;191:153–61.
- [47] Ambrus Z, Balázs N, Alapi T, Wittmann G, Sipos P, Dombi A, et al. Synthesis, structure and photocatalytic properties of Fe(III)-doped TiO<sub>2</sub> prepared from TiCl<sub>3</sub>. *Appl Catal B* 2008;81:27–37.
- [48] Subramanian M, Vijayalakshmi S, Venkataraj S, Jayavel R. Effect of cobalt doping on the structural and optical properties of TiO<sub>2</sub> films prepared by sol-gel process. *Thin Solid Films* 2008;516:3776–82.
- [49] Li G, Dimitrijevic M, Chen L, Rajh T, Gray A. Role of surface/interfacial Cu<sup>2+</sup> sites in the photocatalytic activity of coupled CuO-TiO<sub>2</sub> nanocomposites. *J Phys Chem C* 2008;112:19040–4.
- [50] Fuerte M, Maira AJ, Martínez-Arias A, Fernández-García M, Conesa JC, Soria J. Visible light-activated nanosized doped-TiO<sub>2</sub> photocatalysts. *Chem Commun* 2001;24:2718–9.
- [51] Devi LG, Kumar SG, Murthy BN, Kottam N. Influence of Mn<sup>2+</sup> and Mo<sup>6+</sup> dopants on the phase transformations of TiO<sub>2</sub> lattice and its photo catalytic activity under solar illumination. *Catal Comm* 2009;10:794–8.
- [52] Sharma SD, Saini KK, Kant C, Sharma CP, Jain SC. Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films. *Appl Catal B Environ* 2008;84:233–40.
- [53] Devi L, Kumar G. Influence of physicochemical–electronic properties of transition metal ion doped polycrystalline titania on the photocatalytic degradation of Indigo Carmine and 4-nitrophenol under UV/solar light. *Appl Surf Sci* 2011;257:2779–90.
- [54] Karakitsou E, Verikios E. Effects of alervalent cation doping of TiO<sub>2</sub> on its performance as a photocatalyst for water cleavage. *J Phys Chem* 1993;97:1184–9.
- [55] Maggos Th, Bartzis JG, Leva P, Kotzias D. Application of photocatalytic technology for NO<sub>x</sub> removal. *Appl Phys A* 2007;89:81–4.
- [56] Papadimitriou V, Stefanopoulos V, Romanias M, Papagiannakopoulos P, Sambani K, Tudose V, et al. Determination of photo-catalytic activity of undoped and Mn-doped TiO<sub>2</sub> anatase powders on acetaldehyde under UV and visible light. *Thin Solid Films* 2011;520:1195–201.
- [57] Allen NS, Edge M, Sandoval G, Verran J, Stratton J, Matby J. Photocatalytic coatings for environmental applications. *Photochem Photobiol* 2005;8:279–90.
- [58] Salthammer T, Fuhrmann F. Photocatalytic surface reactions on indoor wall paint. *Environ Sci Technol* 2007;41:6573–8.
- [59] Pichat P. Some views about indoor air photocatalytic treatment using TiO<sub>2</sub>: conceptualization of humidity effects, active oxygen species, problem of C1–C3 carbonyl pollutants. *Appl Catal B, Environ* 2010;99:428–34.
- [60] Gamage J, Zhang Z. Applications of photocatalytic disinfection. *Int J Photoenergy* 2010;1–11.
- [61] Bolashikov ZD, Melikov AK. Methods for air cleaning and protection of building occupants from airborne pathogens. *Build Environ* 2009;44:1378–85.
- [62] Malato S, Maldonado MI, Fernández-Ibáñez P, Oller I, Polo I, Sánchez-Moreno R. Decontamination and disinfection of water by solar photocatalysis: the pilot plants of the Plataforma Solar de Almería. *Mater Sci Semicond Process* 2016;42:15–23.
- [63] Karunakaran C, Vijayabalan Manikandan G, Gomathisankar P. Visible light photocatalytic disinfection of bacteria by Cd–TiO<sub>2</sub>. *Catal Commun* 2001;12:826–9.
- [64] Markowska-Szczupak A, Ulfik K, Morawski AW. The application of titanium dioxide for deactivation of bioparticulates: an overview. *Catal Today* 2011;169:249–57.
- [65] Yoo S, Ghafoor K, Kim S, Sun YW, Kim JU, Yang K, et al. Inactivation of pathogenic bacteria inoculated onto a BactoTM agar model surface using TiO<sub>2</sub>-UVC photocatalysis, UVC and chlorine treatments. *J Appl Microbiol* 2015;119:688–96.
- [66] Venieri D, Fraggadaki A, Kostadima M, Chatzisyneon E, Binas V, Zachopoulos A, et al. Solar light and metal-doped TiO<sub>2</sub> to eliminate water-transmitted bacterial pathogens: photocatalyst characterization and disinfection performance. *Appl Catal B Environ* 2014;154–155:93–101.
- [67] Venieri D, Gounaki I, Binas V, Zachopoulos A, Kiriakidis G, Mantzavinos D. Inactivation of MS2 coliphage in sewage by solar photocatalysis using metal-doped TiO<sub>2</sub>. *Appl Catal B Environ* 2014;178:54–64.
- [68] Venieri D, Gounaki I, Bikouvaraki M, Binas V, Zachopoulos A, Kiriakidis G, et al. Solar photocatalysis as disinfection technique: inactivation of *Klebsiella pneumoniae* in sewage and investigation of changes in antibiotic resistance profile. *J Environ Manag* 2016;1–8. <http://dx.doi.org/10.1016/j.jenvman.2016.06.009>.
- [69] Sánchez B, Sánchez-Muñoz M, Muñoz-Vicente M, Cobas G, Portela R, Suárez S, et al. Photocatalytic elimination of indoor air biological and chemical pollution in realistic conditions. *Chemosphere* 2012;87:625–30.
- [70] Pigeot-Remy S, Real P, Simonet F, Hernandez C, Vallet C, Lazzaroni JC, et al. Inactivation of *Aspergillus niger* spores from indoor air by photocatalytic filters. *Appl Catal B Environ* 2013;134:167–73.
- [71] Jebri S, Hmaied F, Jofre J, MariemYahya, Mendez J, Barkallah I, et al. Effect of gamma irradiation on bacteriophages used as viral indicators. *Water Res* 2013;47:3673–8.
- [72] Gerrity D, Ryu H, Crittenden J, Abbaszadegan M. Photocatalytic inactivation of viruses using titanium dioxide nanoparticles and low-pressure UV light. *J Environ Sci Health A Tox Hazard Subst Environ Eng* 2008;43:1261–70.
- [73] Misstear DB, Gill LW. The inactivation of phages MS2, ΦX174 and PR772 using UV and solar photocatalysis. *J Photochem Photobiol B Biol* 2012;107:1–8.
- [74] Kozlova EA, Safatov AS, Kiselev SA, Marchenko VY, Sergeev AA, Skarnovich MO, et al. Inactivation and mineralization of aerosol deposited model pathogenic microorganisms over TiO<sub>2</sub> and Pt/TiO<sub>2</sub>. *Environ Sci Technol* 2010;44:5121–6.
- [75] Pigeot-Rémy S, Simonet F, Errazuriz-Cerda E, Lazzaroni JC, Atlan D, Guillard C. Photocatalysis and disinfection of water: identification of potential bacterial targets. *Appl Catal B Environ* 2011;104:390–8.
- [76] Chatzisyneon E, Droumpali A, Mantzavinos D, Venieri D. Disinfection of water and wastewater by UV-A and UV-C irradiation: application of real-time PCR method. *Photochem Photobiol Sci* 2011;10:389–95.



**Dr. Vassilios Binas** received his Ph.D. in Chemistry from the University of Crete in 2010. He is currently Researcher in Transparent Conductive Materials Group at the Institute of Electronic Structure and Laser of Foundation for Research and Technology and in Quantum Complexity and Nanotechnology at Department of Physics in University of Crete. His research activities focused on experimental and applied Physics/Chemistry with emphasis on nanostructured materials for energy and environmental applications. Dr. Binas has received a significant number of awards in Competitions of Innovation and Applied Research. He has 3 patents and he has participated to several EU funded research projects. Dr. Binas has been selected as a next generation Young Researcher.



**Dr. Danae Venieri (Assistant Professor)** has been a faculty member in the School of Environmental Engineering at Technical University of Crete and responsible for the establishment of the Laboratory of Environmental Microbiology since 2008. Her research activities focus on the monitoring of aquatic environment in terms of evaluation of microbiological quality and microbial response against pollutants and during disinfection processes. Dr. Venieri has participated to several EU funded research projects and is author/co-author of 45 papers in peer reviewed journals.



**Dr. Dimitrios Kotzias (Ph.D in chemistry)** was Head (retired) of the Chemical Assessment and Testing Unit at the European Commission's Joint Research Centre (JRC)-Institute for Health and Consumer Protection (IHCP). His research activities focused on trace analysis of organic compounds in complex matrices, on photochemical oxidants, on indoor air quality and exposure assessment to chemicals and chemical mixtures. Dr. Kotzias has coordinated/participated of/to several EU funded research projects. Dr. Kotzias is author or co-author of more than 250 papers.



**Prof. George Kiriakidis** obtained his Ph.D. from the University of Salford, UK in 1979. Since 1981 he is a faculty member in the Department of Physics at the University of Crete. He initially served as a research fellow and later as Lecturer and Assistant Professor at the Department of Physics/Applied Physics. He was promoted to an Associate Professor in 2009 and to a Professor in 2015. He is also a senior researcher with IESL/FORTH since 1985, and he is the founder and head of the Photonic and Electronic Materials lab, recently renamed to Transparent Conductive

Materials (TCM) and devices lab. He serves as elected E-MRS vice president since May, 2014. G. Kiriakidis has published more than 100 scientific papers in Refereed Journals and participated in over 80 National and International Conferences (including 40 as invited speaker) He was the chairperson for the TCO2006, TCO2008, TCM2010, TCM2012 and TCM2014 conferences and the Editor and co-author in 7 Scientific Reports and three proceedings books.