

NANOSTRUCTURED METAL OXIDES FOR WASTEWATER DISINFECTION

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2.1 INTRODUCTION

Wastewater generation and release into the environment is a major concern because of its impact on surface and underground water quality. This is particularly important in developing countries where, in many of the cases, domestic and industrial wastewater is discharged into natural water bodies with improper or no treatment. As an example, in Mexico, the annual production of both domestic and industrial wastewater is estimated to be as high as 13.5 km³/year. Only 30% (about 3.9 km³/year) of this wastewater is treated. The estimated amount of pollutants generated is 9 million tons of BOD₅ per year, with only 20% (1.94 million tons of BOD₅) being removed [1].

There may be many different undesirable consequences associated with the release of such significant amounts of contaminants into natural water courses. Among them, probably the most toxic is the dissemination of pathogenic microorganisms causing waterborne diseases through the ingestion of wastewater effluents in the water source downstream. The prevalence of such pathogenic microorganisms in water is probably among the most important human health problems. It is known that unsafe drinking water is related to millions of deaths yearly (around 1,400,000 yearly worldwide) as a result of waterborne diseases [2, 3]. One-sixth of the world's population has been estimated to lack access to water and sanitation services [4] usually associated with poverty [5]. Waterborne diseases affect the poorest sectors of society and are recognized by the United Nations to be the cause of infections for around one billion people in developing countries [6]. Removal of pathogenic microorganisms capable of causing waterborne diseases has become one of the most important scientific and technological tasks, and many different sanitary engineering processes have been developed for achieving this goal [7, 8]. Chlorination is probably the most widely used cost-effective water disinfecting methodology around the world; nevertheless, in some cases chlorination is not capable of inactivating these microorganisms, and it has been associated with unpleasant taste and several concerns on the toxicity of its reaction by-products [9].

Among the alternative methodologies developed to generate safe drinking water, advanced oxidation processes (AOPs) have been identified as emerging technologies for inactivating pathogens in water. Destruction of parasites by applying ozone, ultra-violet (UV) radiation, and homogeneous and heterogeneous photocatalysis (HP) has been discussed in the past for bacteria, fungi, viruses, and other highly resistant microorganisms [10–13]. Among all these interesting alternatives, HP is the technology most extensively discussed in the literature [14] for inactivating microorganisms in water.

2.2 PHOTOACTIVE METAL OXIDES

Photocatalysis is defined as the acceleration of a reaction by using a photocatalyst [15]. The initial step in HP is the absorption of a quantum of energy by the catalyst (usually a semiconductor). Once energy absorption occurs, the catalyzer (C) generates charge carriers (electrons, e^- , and holes, h^+), and excited electrons are transferred to the oxidant (Ox_1). Simultaneously, the catalyzer accepts electrons from the reducer (Red_2) to fill the holes generated at its valence band. Electron flux in both directions is null and the catalyzer remains unaltered as proposed in reaction sequence (2.1) [16]:



HP uses a dispersed solid semiconductor (TiO_2 , ZnO , etc.) to generate a stable colloidal suspension under radiation for stimulating a reaction at the solid/liquid interface. At the interphase between the semiconductor and a solution containing a redox pair, charge transference occurs to balance chemical potentials between the two faces. Metallic oxides and sulfurs are among the most commonly used semiconductor materials available for PC purposes. Nowadays, titanium dioxide (TiO_2) is frequently used as a semiconductor for HP processes and is reported to be among the most active [17]. Table 2.1 gives some of the most common semiconductor materials used in PC reactions, their band-gap energy, and the maximal wavelength values required for catalyst activation.

Degradation of organic pollutants by HP is among the most successful applications of AOPs for eliminating toxic substances in water [18] as suggested by the wide variety of research groups, facilities, scientific reports, and patents around the use of this technology. Use of HP water disinfection has given rise to the design and synthesis of new nanostructured photocatalysts with interesting properties for more efficient environmental applications.

2.3 KINETICS AND REACTION MECHANISMS

For a long time, several groups working on the analysis of HP mechanisms have hypothesized on the photogeneration of holes (h^+) and surface-trapped hydroxyl radicals (HO^\bullet) [19]. Initial steps involved in band-gap irradiation of TiO_2 particles (or any other semiconductor) have been studied in detail by laser-flash photolysis measurements [20, 21]. It is well established that TiO_2 illumination with radiation of the proper wavelength ($\geq E_g$) generates an electron/hole pair that can recombine or dissociate (both reactions are in competition) to produce, in the latter case, a conduction band electron and a valence band hole that are able to migrate to the particle surface. Once on the surface, both charge carriers are able to interact with adsorbed electron acceptors and oxidize electron donors. In the aqueous phase, oxygen is often present as an

TABLE 2.1 Band-gap energy and activation wavelength for some semiconductors [16]

Material	Band-gap energy (eV)	Activation wavelength (nm)
BaTiO ₃	3.3	375
CdO	2.1	590
CdS	2.5	497
CdSe	1.7	730
Fe ₂ O ₃	2.2	565
GaAs	1.4	887
GaP	2.3	540
SnO ₂	3.9	318
SrTiO ₃	3.4	365
TiO ₂	3.2	387
WO ₃	2.8	443
ZnO	3.2	390
ZnS	3.7	336

electron acceptor and HO^\cdot and H_2O are available as electron donors to yield hydroxyl radicals. It is well documented that these trapping reactions occur in a lapse time shorter than 30 ps [22].

Considering the importance of mass transference in the process, initial practical approaches for a quantitative description of HP kinetics have been commonly carried out using a Langmuir–Hinshelwood (L–H) kinetics model [23]. This mathematical model assumes that the reaction occurs on the catalyst surface. According to the L–H model, the reaction rate (r) is proportional to the fraction of particle surface covered by the pollutant (θ_x). Mathematically,

$$r = -\frac{dC}{dt} = k_r \theta_x = \frac{k_r KC}{1 + KC + K_s C_s} \quad (2.2)$$

where k_r is the reaction rate constant, K is the pollutant adsorption constant, C is the pollutant concentration at any time, K_s is the solvent adsorption constant, and C_s is the concentration. During the 1980s, many authors presented their data using the L–H kinetic approach. Nevertheless, despite fitting well with the experimental data, the L–H approach does not consider the role of the radiation field on the mechanism [24, 25].

Other kinetic studies on HP suggest that the reaction rate increases with catalyst concentration to get a maximum value concentration depending on the compound and the reactor used. For these concentrations, the reaction rate remains unchanged or decreases with further increments of catalyst concentration [25]. An interesting problem is the relation between catalyst concentration, reaction rate, radiation absorption, and process improvement. Considering this, many different models have been proposed. Studies have suggested relationships aiming to estimate the radiation absorbed by the catalyst [24, 25]. From these results, several models, most of them based on complex mathematical or statistical computational approaches, have been developed. These models are able to predict radiation absorption and scattering as a function of catalyst concentration, optical path and catalyst type, and its relation to pseudokinetic constants obtained experimentally [24–26]. Based on the radiation absorbed by the catalyst, Alfano's group as well as other authors have focused on the a priori design of photochemical reactors, the improvement of HP reactions, and the generation of intrinsic reaction kinetic that may lead to process scaling-up [27–29].

Besides reactor design, heterogeneous PC degradation reaction can be enhanced by the use of higher active catalyst or inorganic oxidizing species. In the first case, activation of TiO_2 under visible light is a desirable technological approach. In order to utilize visible light for TiO_2 excitation, dye-sensitized and ion-doped TiO_2 has been developed in recent years and has yielded promising results for the photocatalyzed degradation of different substrates [30, 31].

2.4 VISIBLE LIGHT ABSORBING SEMICONDUCTORS

According to reaction sequence (2.1), the production of charge carriers is a fundamental step in the degradation processes using HP. Once generated, these species may lead to hydroxyl radical generation (and the subsequent organic matter degradation) or can recombine to generate the initial state and energy emission. This latter reaction, known as recombination, is a practical problem when using a TiO_2 catalyst, and it is extremely efficient (reaction rate = 10^{-9}s) when no proper electron acceptor is present in the reaction media [32]. This side process is energy-wasting and limits the achievement of high quantum yields (i.e., number of primary chemical reactions per photon absorbed). In most of the cases, dissolved oxygen is used as the electron scavenger, and several works have dealt with its efficiency as an oxidant agent to complete organic matter mineralization [33]. Nevertheless, it has been demonstrated that only low mineralization is reached when dissolved oxygen is used as an oxidant agent [34].

The recombination of charge carriers seriously affects the actual photonic yield of the photocatalyst; however, this is not the only variable related with the effectiveness of the process. One of the main disadvantages in its use is related to the wavelength required for activating TiO_2 . The HP process using titanium dioxide occurs only when it is irradiated with ultraviolet (UV, $\lambda < 400\text{nm}$) radiation and photon energy is absorbed by the crystal structure of the semiconductor, transferring electrons from the valence to the conducting band. This specific characteristic limits the photocatalyst sensitivity when solar radiation is intended to be used since only a small part of the solar spectrum (about 5%) falls within the UV radiation [2, 35]. In order to avoid this limitation, several modifications have been attempted to the TiO_2 PC structure in order to make it active under visible spectral irradiation, improve its photosensitivity and quantum yield, as well as reduce its band-gap energy requirements for PC activation. These modifications follow different approaches: (i) dye sensitization, (ii) TiO_2 coupling with other semiconducting materials with appropriate band-gap energy, (iii) surface deposition of metal clusters, and (iv) doping the crystal lattice with metallic and nonmetallic foreign atoms; see Figure 2.1 [36, 37].

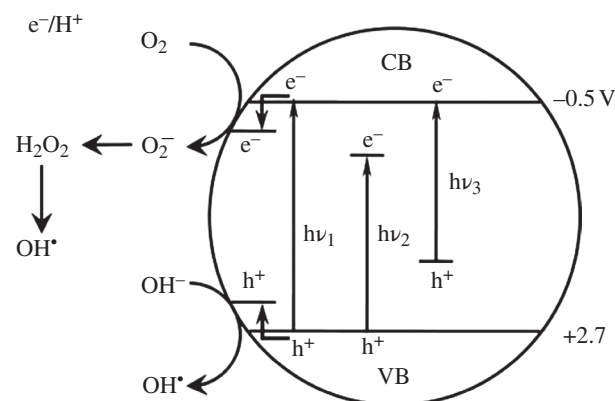


FIGURE 2.1 TiO₂ photocatalyst's band-gap modification for undoped (hν₁), metal doping (hν₂), and nonmetal doping (hν₃).

Several years ago, Sato discovered that the addition of NH₄OH in a titania sol-gel formulation followed by calcination of the precipitated powder at temperatures of 300 °C and higher resulted in a material that exhibited visible light sensitization [38]. It was not until a few years ago that a first explanation of this phenomenon was provided by Asahi and coworkers who reported that nitrogen-doped TiO₂ could absorb in the visible light. It was a yellowish material prepared by sputtering a TiO₂ target under a N₂(40%)/Ar gas mixture followed by annealing under N₂ at 550 °C for 4 h, and it was photocatalytically active for the degradation of methylene blue and acetaldehyde under visible light [39–42].

Nitrogen is one of the most widely reported dopants for shifting TiO₂ spectral absorption into the visible range. Substitution of N in the titania lattice has been proposed to contribute to a narrow band gap by merging nitrogen and oxygen 2p states on the top of the valence band as nitride (Ti–N) or oxynitride (Ti–O–N). Another theory is the formation of oxyanion species at interstitial lattice sites, where N is bonded to one or more oxygen atoms creating localized intergap states. Both arrangements are considered to change the energy phototreshold responsible for the red shift of the optical absorption toward the visible spectra region [43].

Several recent studies in this emerging field of N-doped TiO₂ catalyst activated by visible light deal with the fundamental physics to explain the electronic properties of N-doped TiO₂ [44–46] and provide solid evidence for the promising properties of this environmentally “green” material [47, 48]. However, some other reports have suggested that anion-doped TiO₂ photocatalysts have low efficiency due to charge carrier recombination from anion doping [49] and that metal ion modification influences light absorption and photoreactivity of TiO₂ acting as electron/hole traps [50].

Silver-, vanadium-, iron-, and palladium-modified nitrogen-doped TiO₂ have been tested to enhance titania's PC performance in inactivating Gram-negative bacteria, such as *Escherichia coli*, *Pseudomonas aeruginosa*, and *Prevotella intermedia* [50–55], as well as some Gram-positive bacteria, such as Methicillin-resistant *Staphylococcus aureus* (MRSA), *Staphylococcus epidermidis*, *Staphylococcus saprophyticus*, *Streptococcus pyogenes*, *Staphylococcus aureus*, and *Saccharomyces cerevisiae* [56–59], and a few protozoa, such as *Tetraselmis suecica*, *Amphidinium carterae*, *Chlorella vulgaris* [60, 61], in water.

Nonmetallic ion doping has also been shown to be effective to induce modifications of the electronic structure of TiO₂ by creating surface oxygen vacancies due to charge compensation between the nonmetallic ion and Ti⁴⁺ but without producing a significant change in the optical absorption of the photocatalyst [37, 62]. Moreover, codoping of TiO₂ with nitrogen and fluorine has demonstrated high PC activity in the visible region with beneficial effects induced by both dopants [63–65]. Huang et al. confirmed strong visible light absorption and high PC activity of N–FTiO₂ for *p*-chlorophenol and rhodamine B degradation under visible light irradiation [64]. Xie et al. effectively decomposed methyl orange with a visible light-activated N–F–TiO₂ photocatalyst [65]. Both attributed their findings to the synergistic effect of nitrogen and fluorine doping. More recently, Dionysiou's group has shown the effectiveness of N–TiO₂ in removing cyanobacterial toxins in water by using visible radiation [37, 66]. Castillo-Ledezma et al. have recently demonstrated the capability of N–F–TiO₂ in inactivating *E. coli* using solar radiation under several different reaction conditions, including pH value and radiation wavelengths (visible and UV + visible), and they showed that the N–F–TiO₂ process possesses higher efficiency than the regular TiO₂ and solar disinfection processes [2]. Similar results were found by Wong et al. for nitrogen-doped TiO₂ in inactivating *E. coli* and several other pathogenic microorganisms [67]. They also found that proteins and light-absorbing contaminants reduce the bacterial activity of the photocatalyst as a result of their light-shielding effects. Liu et al. found that extracellular polymeric substances (EPS) generated by some heterotrophic bacteria play an important role in controlling the kinetics of the solar-induced PC process by generating a protective layer against the presence of photogenerated reactive oxygen species (ROS) during the photocatalyst activation [68].

In a very interesting synergistic approach, Wu et al. developed and tested a metal-/nonmetal-doped TiO₂ catalyst for the inactivation of Gram-negative (*E. coli* and *P. aeruginosa*) and Gram-positive (*S. aureus*) cells [69]. They found that by combining both metal and nonmetal dopants, PC activity was much higher than using the dopants separately under visible light illumination.

2.5 SLURRIES OR IMMOBILIZED PHOTOCATALYST

The generation of catalyst sludges as by-products is one of the main disadvantages of HP processes in water treatment. At the pilot-plant level, HP uses suspended TiO₂ in photoreactors where the semiconductor is recovered after the treatment. According to various lab-scale research reports [14], the use of TiO₂ in suspensions is more efficient than their use in immobilized forms. Nevertheless, this latter form possesses specific advantages, such as cost reductions, a decrease in material losses, and the likelihood of skipping recovery steps in the process, which make it possible to produce immobilized titania photocatalysts with higher efficiency as compared with those reported to date [70, 71].

Several supporting materials, from sand to quartz optical fiber, have been reported so far for TiO₂ immobilization. During the past few years, the in situ generation of catalysts seems to be the most promising technology for catalyst immobilization [71]. Other authors [72] have demonstrated that by using this method, the generated fixed form of titanium dioxide presents equal efficiency as Degussa P-25 (considered the most efficient form of titanium dioxide) suspended catalyst for bacteria inactivation. However, more research is needed before this can be considered for the future design of efficient PC processes.

2.6 TiO₂ PARTICLES AND NANOTUBES

Nanostructured TiO₂ with different sizes, shapes, and morphologies (nanoparticles, nanofibers, nanowires, nanorods, nanoporous materials, and nanotubes) have been prepared and their unique properties tested for several applications [73]. The preparation method plays a key role on the variety of structures formed. Some well-known methods to prepare TiO₂ nanostructures are sol-gel, microemulsion, hydrothermal, solvothermal, vapor deposition, and anodization [74, 75]. The main idea behind this molecular design is to improve the physical and chemical properties of TiO₂, including their PC activity and PV response [76].

One of the most promising TiO₂ nanostructures for environmental applications is titanium dioxide nanotubes (TDN). Literature on TDN is the second most abundant only after that on carbon nanotubes. TDNs prepared from the anodization of metal plates have attracted interest because they can improve performance on well-known titania applications such as water photoelectrolysis, photocatalysis, heterojunction solar cells, gas sensing, and environmental purification [77, 78] since they provide a highly ordered TiO₂ nanotubular array with a large specific surface area. Two important structural characteristics of these TDN arrays are their inner diameter of approximately 100 nm and an average length of 3 μ m (Fig. 2.2).

The highly ordered structure can improve the transport of photogenerated electrons in the TiO₂ film by providing a unidirectional electric channel and reducing grain boundaries in photocatalysis and photoelectrochemical applications, while the large surface area can allow more efficient light harvesting [79, 80].

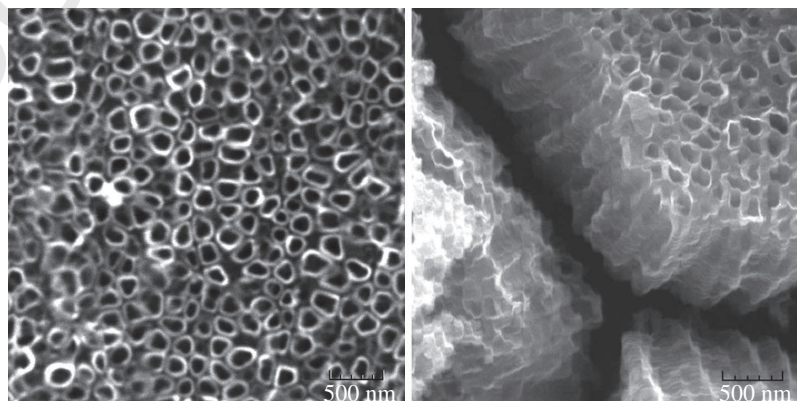


FIGURE 2.2 Standard electron microscope (SEM) images of TDN obtained by anodization. Left top view; right cross-sectional image.

As a material for electrocatalytic oxidation of azo dyes, TDNs show null or very low capability to oxidize them [80]. However, when electrochemical oxidation is combined with UV irradiation, degradation becomes more effective as in the case of methyl orange degradation reported by Zhang, who achieved a degradation efficiency of 56.3% for an irradiation time of 90 min with an initial dye concentration of 2×10^{-4} M [80].

Also, in electrocatalysis, TiO_2 nanotubes have been used as a substrate to support electroactive materials like noble metals (Ag, Au, Pd, Pt, and Ru) [81–83] or metal oxides. As mentioned earlier, TiO_2 itself is a widely used material in electrochemistry due to its semiconductive properties, insertion host capacity, and long-term stability [81]. These characteristics make TDNs very suitable to hold other materials providing a large surface area and a chemically stable structure that can be repeatedly used [83]. Gold nanoparticles (3 nm) loaded on TDN layers have proven to be more effective for the reduction of oxygen than gold nanoparticles dispersed on a compact flat TiO_2 film. Gold as well as other noble metals like silver, palladium, platinum, and ruthenium have been deposited on TDNs in order to enhance TiO_2 PC properties [81].

2.7 PHOTOCATALYSIS ON TiO_2 NANOTUBES

In recent years colloidal and particulated TiO_2 have been used to photodegrade pollutants in both liquid and gas phases. However, these suspended systems must face three inherent technical problems: (i) separation or filtration after the reaction, (ii) particle aggregation, and (iii) the problems associated with continuous flow systems. Methods to prepare TiO_2 on a solid support have been reported, but the efficiency of the immobilized system is much lower than that of suspended ones because of the reduction of surface active area on the immobilized catalyst. Therefore, TiO_2 nanotubes might overcome this drawback due to its high specific surface area [84]. Toward this end, the PC activity of TDNs toward methyl orange discoloration was evaluated and compared with that of a TiO_2 nanoparticle film. In this study, the authors reported a more efficient degradation activity on the nanotubes than on the nanoparticle film. This higher efficiency is attributed to a more effective separation of the photo-generated electron–hole pairs and the higher inner surface area of the nanotube structure [84].

In general, in order to enhance TiO_2 PC activity, a deposit of noble metal particles increases electron–hole separation and promotes electron transfer processes. It has been stated that nanotubes loaded with gold and silver nanoparticles form local Schottky junctions that present a higher potential gradient than at the TiO_2 /electrolyte interface [82]. Photocatalysis can be improved if two metals are simultaneously used to modify TiO_2 as it was investigated for a Au–Pd–comodified TiO_2 nanotube film (Au–Pd– TiO_2). The activities of naked TiO_2 and Au–Pd– TiO_2 toward malathion degradation were compared. The study showed that 73.8% of malathion was removed in the presence of naked TiO_2 , but 98.2% malathion removal was achieved when Au–Pd– TiO_2 was used instead of naked TiO_2 [83].

As we can see, one of the major trends in the environmental use of TiO_2 nanotubes is combining them with another material, metal, or semiconductor in order to enhance their PC properties or to obtain a dual material that has the properties of both parent materials. In some cases, the TiO_2 nanotube array plays the role of a substrate, which has a large surface area, good mechanical resistance, and greater adsorption capacity to support a highly electroactive metal oxide such as PbO_2 (Fig. 2.3a) or SnO_2 doped with Sb (Fig. 2.3b) [85–87].

PbO_2 and SnO_2 are known to have a high oxygen evolution potential, which makes them more efficient for electro-oxidation of organic pollutants. These active oxides loaded on ceramics, Ti, and other support materials are suitable for environmental

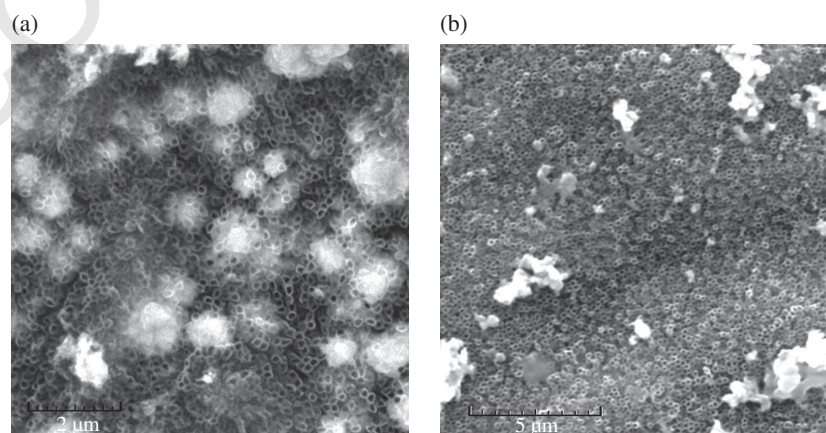


FIGURE 2.3 (a) PbO_2 deposited on TDN; (b) Sb– SnO_2 deposited on TDN.

applications due to their low cost, good corrosion resistance, and high conductivity, but mechanical instability of their coatings is a major disadvantage that has to be overcome. To achieve that goal, several efforts are being made, including the use of TiO₂ nanotubes prepared by the anodization of Ti plates, which provides a stake structure where the electroactive materials can penetrate and combine more firmly, thereby increasing the stability of electrodes [85, 87].

Relatively few works dealing with TDN tests for water disinfection have been reported. Ng et al. synthesized TDNs via electrochemical anodization followed by calcination and used these materials for *E. coli* inactivation in water [88]. They found that over 95% of the initial *E. coli* viable counts were inactivated in only 50 min under UV-A radiation. Presence of ionic species and organic compounds in water did not produce any observable effect in the inactivation rate.

2.8 PHOTOELECTROCATALYSIS ON TDN

The idea of combining TiO₂ with other oxides in order to obtain an electrode that presents both PC and electrocatalytic properties is not new [89]. However, the possibility of using TDNs, prepared anodically on Ti plates, as both support and photoactive material, makes it easier to grow or implant electroactive oxides to create an electrode material with photoelectrocatalytic (PEC) properties. Thus, great attention has been paid recently to prepare electrodes of this type.

The use of naked TDN as photoelectrocatalysts has been reported for azo decolorization, for example, in the cases of methyl orange (MeO) or acid orange 7. In the case of methyl orange, PEC and PC activities of the nanotube electrode were compared for decolorization experiments where a 0.5-V potential was applied and a UV illumination was utilized. A 99.06 % removal was achieved under PEC conditions, while only 21.5% of the MeO was removed by the PC process for a total time of 90 min [80]. For acid orange 7, total removal (discoloration) was achieved after 45 min of PC decomposition under an applied potential of 1.0V versus the Ag/AgCl reference electrode [90]. According to this author, applying an electrochemical potential helps to control the band bending, which can result in more efficient charge carrier separation.

One way to enhance the PEC properties of TDNs is to couple them with other materials like Sb-doped SnO₂, SiO₂, Bi₂O₃, Fe₂O₃, ZnO, and CdS [87, 91, 92]. Thus, for example, a photocatalyst like Bi₂O₃ that is capable of oxidizing water under a visible light irradiation could be loaded onto a TiO₂ nanotube array electrode, and the composite electrode achieved higher catalytic activities toward 2,4-dichlorophenol degradation than the individual Bi₂O₃ or TiO₂ electrode materials did. An effective photocatalyst for the elimination of environmental pollutants should present high PC activity both in the UV and in the visible light regions. This can be accomplished by a composite electrode like Bi₂O₃/TiO₂, where Bi₂O₃ is photoactive under visible light and TiO₂ is active under UV irradiation [87].

PEC using TDN has also been briefly reported for application as a promising and powerful tool for bacteria inactivation [93]. Current work deals with the development of TDN through electrochemical anodization in aqueous solution. The nanotube electrode built by this procedure was compared with a mesoporous TiO₂ electrode for *E. coli* inactivation. High surface TiO₂ nanotubes resulted in high photocurrent and an extremely rapid *E. coli* inactivation rate (~10⁶ CFU mL⁻¹ killed in less than 10 min). Recently, a Ag/AgBr/TiO₂ nanotube array with enhanced visible light activity was synthesized and its PEC activity tested for inactivation of *E. coli* under visible radiation ($\lambda > 400$ nm) resulting in complete sterilization highly superior than with other reference photocatalysts [94]. However, other authors disagree with these results, and there is a controversy on the real advantages of PEC for bacteria inactivation [95].

2.9 OTHER NANOSTRUCTURED METAL OXIDES

Metals have been used in water treatment for long. For example, silver has been in use for the treatment of infections and wounds as well as for water disinfection due to its antimicrobial activity since Roman times. More recently, other metal derivatives, such as metal oxides but also metal chalcogens, have drawn attention because of their potential applications in inhibiting microorganism growth due to their high surface areas, unusual crystal morphologies, and high catalytic activity. The use of oxide nanomaterials for environmental remediation has been reviewed recently [96, 97] and is a hot research field. They can be used for fast and cost-effective cleaning procedures for contaminants in comparison to traditional methods [98, 99]. In particular, the use of nanomaterials for wastewater treatment has attracted the attention of some groups, as there are several reports on the specific biocide action of some nanomaterials against different types of microorganisms that show low general toxic profiles and good stability [100, 101]. This property of nanomaterials may be exploited for use as effective disinfectant agents. It remains a complex issue to understand the several factors involved in toxicity, such as chemical composition, surface reactivity, size, distribution, cell type, experimental setup, as it requires an interdisciplinary view. However, before their large-scale use for water disinfection, it is necessary to understand the real environmental impact that engineered nanomaterials have [98].

Magnesium oxide (MgO) nanoparticles showed biocidal activity against certain Gram-positive and Gram-negative bacteria, as well as spores, in particular against *E. coli*, *B. megaterium*, *Streptococcus pneumoniae*, and *Bacillus subtilis*. [102, 103]. Alumina (aluminum oxide, Al_2O_3) nanoparticles have also shown mild antibacterial activity against *E. coli*, *S. pneumoniae*, *P. aeruginosa*, and *B. subtilis* cultures [104–106]. Bulk versus nanoalumina comparison showed that the nanosized Al_2O_3 had higher toxicity at the same concentration [107, 108].

Copper (II) oxide (CuO) and copper (I) oxide (Cu_2O) are both semiconducting compounds that are cytotoxic to several types of cells [109, 110]. In fact, they are considered among the most toxic nanomaterials based on several studies. In the case of environmental effects, it has been reported that CuO nanoparticles with sizes lesser than 50 nm are toxic when tested against *Nitellopsis obtusa*, *Chlorella*, shrimp *Thamnocephalus platyurus*, and rotifer *Brachionus calyciflorus* [111]. In that sense, copper oxides may be useful for applications in water disinfection. For example, CuO nanoparticles were effective in killing several pathogenic bacteria (*P. aeruginosa*, *Proteus* spp., *B. subtilis*) when used in high concentrations [112]. Several reports relate the toxicity to copper ions more than to the presence of nanoparticles, but sometimes the nature of the specific toxic agent is unclear. Coordinative interactions with chemical moieties with great affinity to copper ions such as carboxylic or amine groups, as well as the probability of intercalation into DNA structures to form complexes with nucleotides, may cause disruption of biochemical process and thus be the reason for their toxicity [113]. Cu_2O nanoparticles supported onto natural clinoptilolite showed 100% antiprotozoan activity against *Paramecium caudatum* and *Eurytemora affinis* after 1 h of contact and inhibitory growth effects on *E. coli* and *S. aureus* in tests specifically designed to measure the effectiveness of these materials for disinfection of secondary effluent water and removal of pathogenic microorganisms in the tertiary stage of wastewater treatment [114].

Zinc oxide (ZnO), on the other hand, has been used in several commercial applications such as in sunscreens, cosmetics, pharmaceutical, and the plastic and food industry due to its semiconducting properties, stability, and antibacterial activity. It has been tested against bacteria such as *B. subtilis*, *E. coli*, *Pseudomonas fluorescens*, *Listeria monocytogenes*, *Salmonella enteritidis*, *Salmonella typhimurium*, and *S. aureus*, showing from mild to strong microbicidal activity, although the studies were more oriented toward finding novel food and agricultural applications than toward finding a utility for wastewater treatment [107, 115–118]. The mechanism of antibacterial activity is suggested to proceed through generation of hydrogen peroxide on the ZnO surface. It has also been suggested that the release of Zn(II) ions may damage the cell membrane, and they may interact with specific biomolecules [119, 120]. Cobalt-doped ZnO antibacterial activity was tested against *E. coli*, *Klebsiella pneumonia*, *Shigella dysenteriae*, *Salmonella typhi*, *P. aeruginosa*, *B. subtilis*, *S. aureus*, and the fungi *Fusarium* sp., showing significant results [121, 122]. The use of thin films of ZnO is also being considered to avoid the growth of biofilms, which may be very useful for wastewater treatment technologies involving large active surfaces or membranes [123].

Cerium oxide (CeO_2) nanoparticles have shown antimicrobial activity by electrostatically binding the cell membrane of Gram-negative cells [124]. They have been detected by monitoring the bacterial growth on a solid medium of *S. aureus*, *P. aeruginosa*, *Klebsiella* sp., *S. pneumoniae*, and *S. aureus* [104, 125]. When compared with bulk and nano CeO_2 , bulk CeO_2 showed less toxicity than their nanosized counterparts [126].

Nitrogen-doped ZrO_2 has been reported to effectively inhibit the growth of *E. coli* and biofilm heterotrophic bacteria under solar light illumination [68]. Iron oxides (FeO , $\alpha\text{-Fe}_2\text{O}_3$, $\beta\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4) are also of chemical interest as they are biocompatible and some of them are magnetically active. They are able to participate in light-driven or pH-induced redox changes that are responsible for the generation of ROS and other highly reactive chemical species (such as primarily hydroxyl radicals), following Fenton-like mechanisms. Just as in the case of TiO_2 , the use of such reactive species for water disinfection is attractive as they are produced by the illumination of a suspension of contaminated water and nanoparticles for a short time, and solar light may be used when the shifting of the optical response from UV to visible light is to be achieved. In that sense, the growth of *S. aureus* cultures was inhibited significantly compared to control samples when 3 mg/ml of iron oxide dose was used [127]. It has also been reported that Fe_3O_4 nanoparticles have an inhibitory effect on *E. coli* in a concentration-dependent manner; although no correlation to light exposition was made, the authors suggested that ROS may be responsible for growth inhibition [128]. However, a recent study warns that superparamagnetic iron oxide nanoparticles (SPIONs) may have a negative effect for wastewater remediation as they induce an increase of *P. aeruginosa* biofilm biomass [129].

2.10 CONCLUSIONS

The specific biocide activity of some nanomaterials against microorganisms present in wastewater is a very attractive property for their eventual incorporation in large-scale methods for water disinfection. However, several important challenges remain with respect to their commercial use. First, it is necessary to remove particles from water as they may negatively interfere in secondary treatment processes or, due to their inherent toxicity, may present a risk for the environment (biomass) or water consumers. Second, electrostatic or van der Waals interactions among nanoparticles to form larger aggregates may be useful

to obtain particle sizes easily trapped by traditional filtration methods or to induce spontaneous precipitation. But then, they may be incorporated into activated sludge, creating another type of problem—affecting microorganisms present there. Their size may also increase due to interactions with organic matter dispersed in solution (humic and fulvic acids, carbonaceous materials, among others). Core-shell nanoparticles involving a ferromagnetic layer is another attractive option as the latter may be used to remove nanoparticles by simply applying a strong external magnetic field. Functionalization of their surfaces to maintain their solubility, increase their stability against aggregation, decrease their chemical reactivity at a wide range of pH values, or avoid interactions with chemical substances present at solution is also key for their eventual consideration in wastewater treatment procedures. Biological interactions with other organisms (not only microbes, but also other phyla such as invertebrates, vertebrates, and plants) may prove to be another challenge, as the nanoparticles may biodegrade, suffering biologically induced chemical and physical transformations, which affects their stability and chemical reactivity, or even changes their biological activity from nontoxic to highly toxic or vice versa.

All these problems make the field more attractive for further research in order to overcome the difficulties and better exploit the unique properties of nanomaterials for wastewater treatment.

REFERENCES

- [1] Comisión Nacional del Agua (CNA). 2011 Water statistics in Mexico. Available at: <http://www.conagua.gob.mx/ocb/ConsultaTemasInteres.aspx?n0=f16ed22d-197b-4b43-bc12-4af596c47ba9> (Accessed March 15, 2013).
- [2] Castillo-Ledezma JH, Sánchez-Salas JL, López-Malo A, Bandala ER. Effect of pH, solar irradiation and semiconductor concentration on the photocatalytic disinfection of *Escherichia coli* in water using Nitrogen-doped TiO₂. *Eur. Food Res. Tech.* 2011;233:825–834.
- [3] Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Mariñas BJ, Mayes AM. Science and technology for water purification in the coming decades. *Nature* 2008;452:302–310.
- [4] Montgomery MA, Elimelech M. Water and sanitation in developing countries: Including health in the equation. *Environ. Sci. Technol.* 2007;41:17–24.
- [5] Gelover S, Gomez L, Reyes K, Leal T. A practical demonstration of water disinfection using TiO₂ films and sunlight. *Water Res.* 2006;40:3274–3280.
- [6] UN. 2012. The millennium development goals report, Available at <http://www.un.org/en/development/desa/publications/mdg-report-2012.html> (Accessed March 11, 2013).
- [7] Bandala, E.R. Castillo-Ledezma, J. Gonzalez, L. Sanchez-Salas, J.L. Solar driven advanced oxidation processes for inactivation of pathogenic microorganisms in water. In *Recent Research Development in Photochemistry and Photobiology*. Volume 8, India: Transworld Research Networks: 2011. p. 1–16.
- [8] Riahi K, Ben Mamou A, Ben Thayer B. Date-palms fiber media filters as a potential technology for tertiary domestic wastewater treatment. *J. Hazard. Mat.* 2009;161:608–613.
- [9] Sichel C, Tello J, Cara M, Fernandez-Ibañez P. Effect of UV solar intensity and dose on the photocatalytic disinfection of bacteria and fungi. *Catal. Today* 2007;129:152–160.
- [10] Orta MT, Martinez J, Monje I, Rojas MN. Destruction of helminth (*Ascaris suum*) eggs by ozone. *Ozone-Sci. Eng.* 2004;26:359–366.
- [11] Alouini Z, Jemli M. Destruction of helminth eggs by photosensitized porphyrin. *J. Environ. Monitor.* 2004;3:548–551.
- [12] Bandala ER, Corona-Vasquez B, Guisar R, Uscanga M. Inactivation of highly resistant microorganisms in water using solar driven photocatalytic processes. *Int. J. Chem. React. Eng.* 2009;7:A7.
- [13] Guisar R, Herrera MI, Bandala ER, García J, Corona-Vasquez B. Inactivation of waterborne pathogens using solar photocatalysis. *J. Adv. Oxid. Technol.* 2007;10:453–438.
- [14] McGuigan KG, Conroy RM, Mosler H, Du Preez M, Ubomba-Jaswa E, Fernandez-Ibañez P. Solar water disinfection (SODIS): A review from bench-top to roof-top. *J. Hazard Mater* 2012;235/236:29–46.
- [15] Kish H. What is photocatalysis? In: Serpone N, Pelizzetti E, editors. *Photocatalysis Fundamentals and Applications*. New York: John Wiley and Sons; 1989.
- [16] Malato S. *Solar Photocatalytic Decomposition of Pentachlorophenol Dissolved in Water*. Madrid, Spain: Editorial CIEMAT; 1999.
- [17] Blanco J, Fernandez P, Malato S. Solar photocatalytic detoxification and disinfection of water: Recent overview. *J Solar Energy Eng Trans ASME*, 2007;129:4–15.
- [18] Bandala ER, Estrada C. Comparison of solar collection geometries for application to photocatalytic degradation of organic contaminants. *J. Sol. Energ.-T. ASME* 2007;129:22–26.
- [19] Romero M, Blanco J, Sánchez B, Vidal A, Malato S, Cardona AI, Garcia E. Solar photocatalytic degradation of water and air pollutants: challenges and perspectives. *Sol. Energy* 1999;66:169–182.

- [20] Bahnemann DW, Hilgendorff M, Memming R. Charge carriers dynamic at TiO_2 particles: Reactivity of free and trapped holes. *J. Phys. Chem. B* 1997;101:4265–4275.
- [21] Serpone N. Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. *EPA Newsletter* 1996;58:54–81.
- [22] Serpone N, Lawless D, Khairutdinov R, Pelizzetti E. Subnanosecond relaxation dynamics in TiO_2 colloidal sols (Particle size = 1.0–13.4 nm). Relevance to heterogeneous photocatalysis. *J. Phys. Chem.* 1995;99:16655–16661.
- [23] a) Al-Ekabi H, Serpone N. Kinetic studies in heterogeneous photocatalysis. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO_2 supported on a glass matrix. *J. Phys. Chem.* 1988;92:5726–5731.
b) Al-Ekabi H, Serpone N, Pelizzetti E, Minero C, Fox MA, Barton R. Kinetics studies in heterogeneous photocatalysis. TiO_2 -mediated degradation of 4-chlorophenol alone and in three-component mixture of 4-chlorophenol, 2,4-dichlorophenol and 2,4,5-trichlorophenol in air-equilibrated aqueous media. *Langmuir* 1989;5:250–255.
- [24] Bandala ER, Arancibia C, Orozco S, Estrada C. Solar photoreactors comparison based on oxalic acid photocatalytic degradation. *Sol. Energy* 2004;77:509–512.
- [25] Arancibia C, Bandala ER, Estrada C. Radiation absorption and rate constants for carbaryl photocatalytic degradation in a solar collector. *Catal. Today* 2002;76:149–159.
- [26] Curcio D, Gimenez J, Addardak A, Cervera S, Esplugas S. Effects of radiation absorption and catalyst concentration on the photocatalytic degradation of pollutants. *Catal. Today* 2002;75:177–188.
- [27] Alfano OM, Bahnemann D, Cassano AE, Dillert R, Goslich R. Photocatalysis in water environments using artificial and solar light. *Catal. Today* 2000;58:199–230.
- [28] Cassano AE, Alfano OM. Reaction engineering of suspended solid heterogeneous photocatalytic reactors. *Catal. Today* 2000;58:167–197.
- [29] Brandi R, Alfano OM, Cassano AE. Evaluation of radiation absorption in slurry photocatalytic reactors 1. Assessment of methods in use and new proposals. *Environ. Sci. Technol.* 2000;34:2631–2639.
- [30] Bae E, Choi W. Highly enhanced photoreductive degradation of perchlorinated compounds on dye-sensitized metal/ TiO_2 under visible light. *Environ. Sci. Technol.* 2003;37:147–152.
- [31] Lin YM, Tseng YH, Huang JH, Chao CC, Chen CC, Wang I. Photocatalytic activity for degradation of nitrogen oxides over visible light responsive titania-based photocatalyst. *Environ. Sci. Technol.* 2006;40:1616–1621.
- [32] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 1995;95:69–96.
- [33] Martin ST, Lee AT, Hoffmann MR. Photocatalytic degradation of pesticide-acaricides in aqueous suspensions of TiO_2 . *Environ. Sci. Technol.* 1995;29:2567–2573.
- [34] Minero C, Pelizzetti E, Malato S, Blanco J. Large solar plant photocatalytic water decontamination: Effect of operational parameters. *Sol. Energy* 1996;56:421–428.
- [35] Srinivasan C, Somasundaram N. Bactericidal and detoxification effects of irradiated semiconductor catalyst, TiO_2 . *Curr. Sci. India* 2003;85:1431–1438.
- [36] Popa M, Diamandescu L, Vasiliu F, Teodorescu CM, Cosocanu V, Baia M, Feder M, Baia L, Danciu V. Synthesis, structural characterization and photocatalytic properties of iron-doped TiO_2 aerogels. *J. Mater. Sci.* 2009;44:358–364.
- [37] Pelaez MA, de la Cruz AA, Stathatos E, Falaras P, Dionysiou DD. Visible light activated N-F-codoped TiO_2 nanoparticles for the photocatalytic degradation of microcystin-LR in water. *Catal. Today* 2009;144:19–25.
- [38] Sato S. Photocatalytic Activity of NO_x -Doped TiO_2 in the Visible Light region. *Chem. Phys. Lett.* 1986;123:126–128.
- [39] Asahi R, Morikawa T, Ohwaki T, Aoki L, Taga Y. Visible-light photocatalyst in nitrogen-doped titanium dioxides. *Science* 2001;293:269–271.
- [40] Sato S, Nakamura R, Abe S. Visible-light Sensitization of TiO_2 Photocatalysts by Wet-method N doping. *App. Catal. A-Gen.* 2005;284:131–137.
- [41] Morikawa T, Asahi R, Ohwaki T, Aoki K, Taga Y. Band-gap Narrowing of Titanium Dioxide by Nitrogen Doping. *Jpn. J. Appl. Phys.* 2, 2001;40:L561–L563.
- [42] Premkumar J. Development of Super-Hydrophilicity on Nitrogen-Doped TiO_2 Thin Film Surface by Photoelectrochemical Method under Visible Light. *Chem. Mater.* 2004;16:3980–3981.
- [43] Emeline, A.V.; Kuznetsov, V.N.; Rybchuk, V.K.; Serpone, N. Visible light active titania photocatalyst: The case of N-doped TiO_2 -properties and some fundamental issues. *Int. J. Photoenergy*, 2008, 1–19.
- [44] Wang ZP, Cai WM, Hong XT, Zhao XL, Xu F, Cai CG. Photocatalytic Degradation of Phenol in Aqueous Nitrogen-doped TiO_2 Suspensions with Various Light Sources. *Appl. Catal. B-Environ.* 2005;57:223–231.
- [45] Miyauchi M, Ikezawa A, Tobimatsu H, Irie H, Hashimoto K. Zeta Potential and Photocatalytic Activity of Nitrogen Doped TiO_2 Thin Films. *Phys. Chem. Chem. Phys.* 2004;6:865–870.
- [46] Burda C, Lou YB, Chen XB, Samia ACS, Stout J, Gole JL. Enhanced Nitrogen Doping in TiO_2 Nanoparticles. *Nano Letters* 2003;3:1049–1051.

- [47] Gole JL, Stout JD, Burda C, Lou YB, Chen XB. Highly Efficient Formation of Visible Light Tunable $\text{TiO}_{2-x}\text{N}_x$ Photocatalysts and their Transformation at the Nanoscale. *J. Phys. Chem. B* 2004;108:1230–1240.
- [48] Kisch H, Macyk W. Visible-light Photocatalysis by Modified Titania. *ChemPhysChem* 2002;3:399–400.
- [49] Torres GR, Lindgren T, Lu J, Granqvist CG, Lindquist SE. Photoelectrochemical study of nitrogen-doped titanium dioxide for water oxidation. *J. Phys. Chem. B* 2004;108:5995–6003.
- [50] Li Q, Wu P, Xie R, Shang JK. Enhanced photocatalytic disinfection of microorganisms by transition metal ion modification of nitrogen doped titanium oxide. *J. Mater. Res.* 2010;25:167–176.
- [51] a) Wu P, Xie R, Shang JK. Enhanced visible-light photocatalytic disinfection of bacteria spores by palladium-modified nitrogen-doped titanium oxide. *J. Am. Ceram. Soc.* 2008;91:2957–2962.
b) Wu P, Xie R, Imlay K, Shang JK. Visible light induced bactericidal activity of titanium dioxide co-doped with nitrogen and silver. *Environ. Sci. Technol.* 2010;44:6992–6997.
- [52] Sun C, Li Q, Gao S, Cao L, Shang JK. Enhanced photocatalytic disinfection of *Escherichia coli* bacteria by silver modification of nitrogen-doped titanium oxide nanoparticle photocatalyst under visible-light illumination. *J. Am. Ceram. Soc.* 2010; 93:3880–3885.
- [53] Ubongchonlakate K, Sikong L, Saito F. Photocatalytic disinfection of *P. aeruginosa* bacterial Ag-doped TiO_2 film. *Procedia Eng.* 2012;32:656–662.
- [54] Nair RG, Roy J, Samdarshi SK, Mukherjee AK. Mixed phase V doped titania shows high photoactivity for disinfection of *Escherichia coli* and detoxification of phenol. *Sol Energy. Mat. Sol. C.* 2012;105:103–108.
- [55] Mo AC, Xu W, Xian S, Li Y, Bai S. Antibacterial activity of silver-hydroxyapatite/titania nanocomposite coating on titanium against oral bacteria. *Key Eng. Mat.* 2007;330/332:455–458.
- [56] Sheel, D.W.; Brook, L.A.; Ditta, I.B.; Evans, P.; Foster, H.A.; Steele, A.; Yates, H.M. Biocidal silver and silver/titania composite films grown by chemical vapor deposition. *Int. J. Photoenergy*, 2008, article ID 168185, 11p.
- [57] Chen WJ, Tsai PJ, Chen YC. Functional $\text{Fe}_3\text{O}_4/\text{TiO}_2$ core/shell magnetic nanoparticles as photokilling agents for pathogenic bacteria. *Small* 2008;4:485–491.
- [58] Lu JW, Li FB, Guo T, Lin LW, Hou MF, Liu TX. TiO_2 photocatalytic antifungal technique for crop diseases control. *J. Environ. Sci.-China* 2006;18:397–401.
- [59] Erkam A, Bakir U, Karakas G. Photocatalytic microbial inactivation over Pd doped SnO_2 and TiO_2 thin films. *J. Photochem. Photobiol. A* 2006;184:313–321.
- [60] Rodriguez-Gonzalez V, Alfaro SO, Torrez-Martinez LM, Cho SH, Lee SW. Silver- TiO_2 nanocomposites: Synthesis and harmful algae bloom UV photoelimination. *Appl. Catal. B-Environ.* 2010;98:229–234.
- [61] Foster HA, Ditta IB, Varghese S, Steele A. Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity. *Appl. Microbiol. Biot.* 2011;90:1847–1868.
- [62] Reginfo JA, Pulgarin C. Photocatalytic activity of N, S co-doped and N-doped commercial anatase TiO_2 powders towards phenol oxidation and E. coli inactivation under simulated solar light irradiation. *Sol. Energy* 2010;84:37–43.
- [63] Li D, Ohashi N, Hishita S, Kolodiazhyi T, Haneda H. Origin of visible-light-driven photocatalysis: A comparative study on N/F doped and N-F codoped TiO_2 powders by means of experimental characterizations and theoretical calculations. *J. Solid. State Chem.* 2005;178:3293–3302.
- [64] Huang DG, Liao SJ, Liu JM, Dang J, Petrik L. Preparation of visible-light responsive N-F codoped TiO_2 photocatalyst by a sol-gel-solvothermal method. *J. Photoch. Photobio. A* 2006;184:282–288.
- [65] Xie Y, Li Y, Zhao X. Low temperature preparation and visible light induced catalytic activity of anatase N-F codoped TiO_2 . *J. Mol. Catal. A-Chem.* 2007;277:119–126.
- [66] Choi H, Antoniou MG, Pelaez M, de la Cruz AA, Shoemaker JA, Dionysiou DD. Mesoporous Nitrogen-doped TiO_2 for the Photocatalytic Destruction of the Cyanobacterial Toxin Microcystin-LR under Visible Light. *Environ. Sci. Technol.* 2007;41:7530–7535.
- [67] Wong MS, Chu WC, Sun DS, Huang HS, Chen JH, Tsai PJ, Lin NT, Yu MS, Hsu SF, Wang SL, Chang HH. Visible-light-induced bactericidal activity of a nitrogen-doped titanium photocatalyst against human pathogens. *Appl. Environ. Microb.* 2006;72:611–6116.
- [68] Liu Y, Li J, Qiu X, Burda C. Bactericidal activity of nitrogen-doped metal oxide nanocatalysts and the influence of bacterial extracellular polymeric substances (EPS). *J. Photoch. Photobio. A* 2007;190:94–100.
- [69] Wu P, Xie R, Imlay JA, Shang JK. Visible light induced photocatalytic inactivation of bacteria by composite photocatalysts of palladium oxide and nitrogen-doped titanium oxide. *Appl. Catal. B* 2009;88:576–581.
- [70] Balasubramanian G, Dionysiou DD, Suidan MT, Baudin I, Laine JM. Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. *Appl. Catal. B-Environ.* 2004;47:73–84.
- [71] Gelover S, Mondragon P, Jimenez A. Titanium dioxide sol-gel deposited over glass and its applications as photocatalyst for water decontamination. *J. Photoch. Photobio. A* 2004;165:241–246.
- [72] Guillard C, Disdier J, Monnet C, Dussaud J, Malato S, Blanco J, Maldonado MI, Herrmann JM. Solar efficiency of a new deposited titania catalyst: chlorophenol, pesticide and dye removal applications. *Appl. Catal. B-Environ.* 2003;46:319–332.

- [73] Chuangchote S, Jitputti J, Sagawa T, Yoshikawa S. Photocatalytic Activity for Hydrogen Evolution of Electrospun TiO₂ Nanofibers. *ACS Appl. Mater Interfaces* 2009;5:1140–1143.
- [74] Wang J, Zhao L, Lin V, Lin Z. Formation of various TiO₂ nanostructures form electrochemically anodized titanium. *J. Mater. Chem.* 2009;19:3682–3687.
- [75] Hahn R, Macak JM, Schmuki P. Rapid anodic growth of TiO₂ and WO₃ nanotubes in fluoride free electrolytes. *Electrochem. Commun.* 2007;9:947–952.
- [76] Kamat, P. TiO₂ Nanostructures: Recent Physical Chemistry Advances. *The J. Phys. Chem. C*, 2012, 116, 11849–11851.
- [77] Zhang H, Quan X, Chen S, Zhao H. Fabrication and Characterization of Silica/Titania Nanotubes Composite Membrane with Photocatalytic Capability. *Environ. Sci. Technol.* 2006;40:6104–6109.
- [78] Sun W, Yu Y, Pan H, Gao X, Chen Q, Peng L. Cds Quantum Dots Sensitized TiO₂ Nanotube-Array Photoelectrodes. *J. Am. Chem. Soc.* 2008;130:1124–1125.
- [79] Liu Z, Zhang X, Nishimoto S, Jing M, Tryk D, Murakami T, Fujishima A. Highly Ordered TiO₂ Nanotube Arrays with Controllable Length for Photoelectrocatalytic Degradation of Phenol. *J. Phys. Chem. C* 2008;112:253–259.
- [80] Zhang Z, Yuan Y, Shi G, Fang Y, Liang L, Ding H, Jin L. Photoelectrocatalytic Activity of Highly Ordered TiO₂ Nanotube Arrays Electrode for Azo Dye Degradation. *Environ. Sci. Technol.* 2007;41:6259–6263.
- [81] Macak J, Schmidt-Stein F, Schmuki P. Efficient oxygen reduction on layers of ordered TiO₂ nanotubes loaded with Au nanoparticles. *Electrochem. Commun.* 2007;9:1783–1787.
- [82] Paramasivam I, Macak J, Schmuki P. Photocatalytic activity of TiO₂ nanotube layers loaded with Ag and Au nanoparticles. *Electrochem. Commun.* 2008;10:71–75.
- [83] Yu H, Wang X, Sun H, Huo M. Photocatalytic degradation of malathion in aqueous solutions using an Au-Pd-TiO₂ nanotube film. *J. Hazard. Mater.* 2010;184:753–758.
- [84] Zhuang H, Lin C, Lai Y, Sun L, Li J. Some Critical Structure Factors of Titanium Oxide Nanotube Array in its Photocatalytic Activity. *Environ. Sci. Technol.* 2007;41:4735–4740.
- [85] Zhao G, Cui X, Liu M, Li P, Zhang Y, Cao T, Li H, Lei Y, Liu L, Li D. Electrochemical Degradation of Refractory Pollutant Using a Novel Microstructured TiO₂ Nanotubes/Sb-Doped SnO₂ electrode. *Environ. Sci. Technol.* 2009;43:1480–1486.
- [86] Li P, Zhao G, Cui X, Zhang Y, Tang Y. Constructing Stake Structured TiO₂-Nts/Sb-doped SnO₂ Electrode Simultaneously with High Electrocatalytic and Photocatalytic Performance for Complete Mineralization of Refractory Aromatic Acid. *J. Phys. Chem. C* 2009;113:2375–2383.
- [87] Zhao X, Liu H, Qu J. Photoelectrocatalytic degradation of organic contaminants at Bi₂O₃/TiO₂ nanotube array electrode. *Applied Surface Science.* 2011;257:4621–4624.
- [88] Ng J, Zhang X, Zhang T, Pou J, Du JA, Sun D. Construction of self-organized free-standing TiO₂ nanotube arrays for effective disinfection of drinking water. *J. Chem. Technol. Biotechnol.* 2010;85:1061–1066.
- [89] Li J, Zhen L, Li L, Shi G, Xian Y, Jin L. Photoelectro-Synergistic Catalysis at Ti/TiO₂/PbO₂ Electrode and Its Applications on Determination of Chemical Oxygen Demand. *Electroanal.* 2006;18:2251–2256.
- [90] Zlamal M, Macak J, Schmuki P, Krýsa J. Electrochemically assisted photocatalysis on self-organized TiO₂ nanotubes. *Electrochem. Commun.* 2007;9:2822–2826.
- [91] Jeon T, Choi W, Park H. Photoelectrochemical and Photocatalytic Behaviors of Hematite-Decorated Titania Nanotube Arrays: Energy Level Mismatch versus Surface Specific Reactivity. *J. Phys. Chem. C* 2011;115:7134–7142.
- [92] Zhang Y, Zhao G, Lei Y, Li P, Li M, Jin Y, Lv B. CdS-Encapsulated TiO₂ Nanotube Arrays Lidded with ZnO Nanorod Layers and Their Photoelectrocatalytic Applications. *ChemPhysChem.* 2010;11:3491–3498.
- [93] Baram N, Starosvetsky D, Starosvetsky J, Epshtein M, Armon R, Ein-El Y. Enhanced inactivation of *E. coli* bacteria using immobilized porous TiO₂ photoelectrocatalysis. *Electrochim. Acta* 2009;54:3381–3386.
- [94] Hou Y, Li H, Zhao Q, Chen G, Raston CL. Role of hydroxyl radicals and mechanisms of *Escherichia coli* inactivation on Ag/AgBr/TiO₂ nanotube array electrode under visible light irradiation. *Environ. Sci. Technol.* 2012;46:4042–4050.
- [95] Egerton TA. Does PEC by TiO₂ work? *J. Chem. Technol. Biotechnol.* 2011;86:1024–1031.
- [96] Tiwari DK, Behari J, Sen P. Application of nanoparticles in waste water treatment. *World. Appl. Sci. J.* 2008;3:417–433.
- [97] Khin MM, Nair AS, Babu VJ, Murugan R, Ramakrishna S. A review on nanomaterials for environmental remediation. *Energy Environ. Sci.* 2012;5:8075–8109.
- [98] Brar SK, Verma M, Tyagi RD, Surampalli RY. Engineered nanoparticles in wastewater and wastewater sludge – Evidence and impacts. *Waste Manage.* 2010;30:504–520.
- [99] Hajipour MJ, Fromm KM, Ashkarran AA, de Aberastruri DJ, de Larramendi IR, Rojo T, Serpooshan V, Parak WJ, Mahmoudi M. Antibacterial properties of nanoparticles. *Trends Biotechnol.* 2012;30:499–511.

- [100] Li Q, Mahendra S, Lyon DY, Brunet L, Liga MV, Li D, Alvarez PJJ. Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Res.* 2008;42:4591–4602.
- [101] Taylor E, Webster TJ. Reducing infections through nanotechnology and nanoparticles. *Int. J. Nanomedicine* 2011;6:1463–1473.
- [102] Koper O, Klabunde J, Marchin G, Klabunde KJ, Stoimenov P, Bohra L. Nanoscale Powders and Formulations with Biocidal Activity Toward Spores and Vegetative Cells of *Bacillus* Species, Viruses, and Toxins. *Curr. Microbiol.* 2002;44:49–55.
- [103] Ravishankar RV, Jamuna BA. Nanoparticles and their potential application as antimicrobials. In: Mendez-Vilas A, editor. *Science against microbial pathogens: communicating current research and technological advances*. Extremadura, Spain: Formatex Research Center; 2011. p 197–209.
- [104] Gokulakrishnam R, Ravikumar S, Raj JA. *In vitro* antibacterial potential of metal oxide nanoparticles against antibiotic resistant bacterial pathogens. *Asian Pac. J. Trop. Med.* 2012;2:411–413.
- [105] Sadiq M, Chowdhury B, Chandrasekaran N, Mukherjee A. Antimicrobial sensitivity of *Escherichia coli* to alumina nanoparticles. *Nanomed. Nanotechnol.* 2009;5:282–286.
- [106] Mukherjee A, Mohammed SI, Prathna TC, Chandrasekaran N. Antimicrobial activity of aluminum oxide nanoparticles for potential clinical applications. In: Mendez-Vilas A, editor. *Science against microbial pathogens: communicating current research and technological advances*. Extremadura, Spain: Formatex Research Center; 2011. p 245–251.
- [107] Jiang W, Mashayekhi H, Xing B. Bacterial toxicity comparison between nano- and micro-scaled oxide particles. *Environ. Pollut.* 2009;157:1619–1625.
- [108] Balasubramanyam A, Sailaja N, Mahboob M, Rahman MF, Hussain SM, Grover P. *In vitro* mutagenicity assessment of aluminium oxide nanomaterials using the *Salmonella*/microsome assay. *Toxicol. in Vitro* 2010;24:1871–1876.
- [109] Fahmy B, Cormier SA. Copper oxide nanoparticles induce oxidative stress and cytotoxicity in airway epithelial cells. *Toxicol. in Vitro* 2009;23:1365–1371.
- [110] Karlsson HL, Cronholm P, Gustafsson J, Möller L. Copper oxide nanoparticles are highly toxic: a comparison between metal oxide nanoparticles and carbon nanotubes. *Chem. Res. Toxicol.* 2008;21:1726–1732.
- [111] Manusadzianas L, Caillet C, Fachetti L, Gylte B, Grigutyte R, Jurkoniene S, Kartonas R, Sadauskas K, Thomas F, Vitkus R, Féraud J-F. Toxicity of copper oxide nanoparticle suspensions to aquatic biota. *Environ. Toxicol. Chem.* 2012;31:108–114.
- [112] Ren G, Hu D, Cheng EWC, Vargas-Reus MA, Reip P, Allaker RP. Characterization of copper oxide nanoparticles for antimicrobial applications. *Int. J. Antimicrob. Ag.* 2009;33:587–590.
- [113] Rupareli JP, Chatterjee AK, Duttagupta SP, Mukherji S. Strain specificity in antimicrobial activity of silver and copper nanoparticles. *Acta Biomater* 2008;4:707–771.
- [114] Hrenovic J, Milenkovic J, Daneu N, Kepcija RM, Rajic N. Antimicrobial activity of metal oxide nanoparticles supported onto natural clinoptilolite. *Chemosphere* 2012;88:1103–1107.
- [115] Franklin NM, Rogers NJ, Apte SC, Batley GE, Gadd GE, Casey PS. Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl₂ to a freshwater microalga (*Pseudokirchneriella subcapitata*): the importance of particle solubility. *Environ. Sci. Technol.* 2007;41:8484–8490.
- [116] Gordon T, Perlstein B, Houbara O, Felner I, Banin E, Margel S. Synthesis and characterization of zinc/iron oxide composite nanoparticles and their antibacterial properties. *Colloid. Surface A* 2011;1/8:374–379.
- [117] Liu Y, He L, Mustapha A, Li H, Hu ZQ, Lin M. Antibacterial activities of zinc oxide nanoparticles against *Escherichia coli* O157:H7. *J. Appl. Microbiol.* 2009;107:1193–1201.
- [118] Jin T, Sun D, Su Y, Zhang H, Sue HJ. Antimicrobial efficacy of zinc oxide quantum dots against *Listeria monocytogenes*, *Salmonella enteritidis* and *Escherichia coli* O157:H7. *J. Food. Sci.* 2009;74:46–52.
- [119] Brayner R, Ferrari-Iliou R, Brivois N, Djediat S, Benedetti MF, Fievet F. Toxicological impact studies based on *Escherichia coli* bacteria in ultrafine ZnO nanoparticles colloidal medium. *Nano Letters* 2006;6:866–870.
- [120] Huang Z, Zheng X, Yan D, Yin G, Liao X, Kang Y, Yao Y, Huang D, Hao B. Toxicological effect of ZnO nanoparticles based on bacteria. *Langmuir* 2008;24:4140–4144.
- [121] Sharma D, Rajput J, Kaith BS, Kaur M, Sharma S. Synthesis of ZnO nanoparticles and study of their antibacterial and antifungal properties. *Thin Solid Films* 2010;519:1224–1229.
- [122] Nair MG, Nirmala M, Rekha K, Anukalini A. Structural, optical, photo catalytic and antibacterial activity of ZnO and Co doped ZnO nanoparticles. *Mater. Lett.* 2011;65:1797–1800.
- [123] Jones N, Ray B, Ranjit KT, Manna AC. Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. *FEMS Microbiol. Lett.* 2008;279:71–76.
- [124] Thill A, Zeyons O, Spalla O, Chauvat F, Rose J, Auffan M, Flank AM. Cytotoxicity of CeO₂ nanoparticles for *Escherichia coli*: Physico-chemical insight of the toxicity mechanism. *Environ. Sci. Technol.* 2006;40:6151–6156.

- [125] Negahdary M, Mohseni G, Fazilati M, Parsania S, Rahimi G, Rad S, Rezaei-Zarchi S. The antibacterial effect of cerium oxide nanoparticles on *Staphylococcus aureus* bacteria. *Ann. Biol. Res.* 2012;3:3671–3678.
- [126] Kuang Y, He X, Zhang Z, Li Y, Zhang H, Ma Y, Wu Z, Chai Z. Comparison study on the antibacterial activity of nano- or bulk-cerium oxide. *J. Nanosci. Nanotechnol.* 2011;11:4103–4108.
- [127] Tran N, Mir A, Mallik D, Sinha A, Nayar S, Webster TJ. Bactericidal effect of iron oxide nanoparticles on *Staphylococcus aureus*. *Int. J. Nanomedicine* 2010;5:277–283.
- [128] Chatterjee S, Bandyopadhyay A, Sarkar K. Effect of iron oxide and gold nanoparticles on bacterial growth leading towards biological application. *J. Nanobiotechnol.* 2011;9:1–7.
- [129] Haney C, Rowe JJ, Robinson JB. SPIONs increase biofilm formation by *Pseudomonas aeruginosa*. *J. Biomater. Nanobiotechnol.* 2012;3:508–518.