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## 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 km<sup>3</sup>/year. Only 30% (about 3.9 km<sup>3</sup>/year) of this wastewater is treated. The estimated amount of pollutants generated is 9 million tons of BOD<sub>5</sub> per year, with only 20% (1.94 million tons of BOD<sub>5</sub>) 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, ultraviolet (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 <sub>3</sub>	3.3	375
CdO	2.1	590
CdS	2.5	497
CdSe	1.7	730
Fe <sub>2</sub> O <sub>3</sub>	2.2	565
GaAs	1.4	887
GaP	2.3	540
SnO <sub>2</sub>	3.9	318
SrTiO <sub>3</sub>	3.4	365
TiO <sub>2</sub>	3.2	387
WO <sub>3</sub>	2.8	443
ZnO	3.2	390
ZnS	3.7	336

electron acceptor and  $\text{HO}^-$  and  $\text{H}_2\text{O}$  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 ( $\theta_x$ ). Mathematically,

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

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].

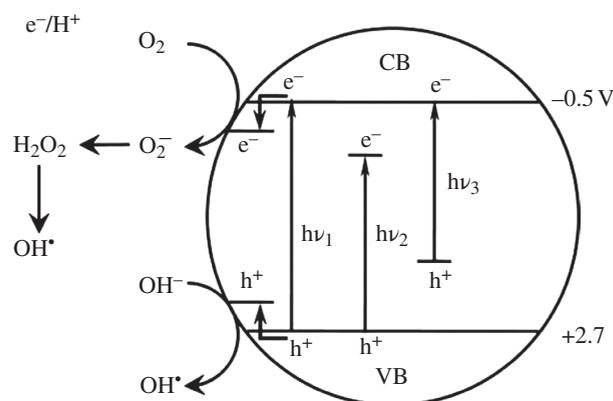
Other kinetic studies on HP suggest that the reaction rate increases with catalyst concentration to get a maximum value concentration depending on the compound and the reactor used. For these concentrations, the reaction rate remains unchanged or decreases with further increments of catalyst concentration [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  $\text{TiO}_2$  under visible light is a desirable technological approach. In order to utilize visible light for  $\text{TiO}_2$  excitation, dye-sensitized and ion-doped  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$ . The HP process using titanium dioxide occurs only when it is irradiated with ultraviolet (UV,  $\lambda < 400$  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  $\text{TiO}_2$  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)  $\text{TiO}_2$  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** TiO<sub>2</sub> photocatalyst's band-gap modification for undoped ( $h\nu_1$ ), metal doping ( $h\nu_2$ ), and nonmetal doping ( $h\nu_3$ ).

Several years ago, Sato discovered that the addition of NH<sub>4</sub>OH 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 TiO<sub>2</sub> could absorb in the visible light. It was a yellowish material prepared by sputtering a TiO<sub>2</sub> target under a N<sub>2</sub>(40%)/Ar gas mixture followed by annealing under N<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> catalyst activated by visible light deal with the fundamental physics to explain the electronic properties of N-doped TiO<sub>2</sub> [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 TiO<sub>2</sub> photocatalysts have low efficiency due to charge carrier recombination from anion doping [49] and that metal ion modification influences light absorption and photoreactivity of TiO<sub>2</sub> acting as electron/hole traps [50].

Silver-, vanadium-, iron-, and palladium-modified nitrogen-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> by creating surface oxygen vacancies due to charge compensation between the nonmetallic ion and Ti<sup>4+</sup> but without producing a significant change in the optical absorption of the photocatalyst [37, 62]. Moreover, codoping of TiO<sub>2</sub> 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–FTiO<sub>2</sub> 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–TiO<sub>2</sub> 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–TiO<sub>2</sub> in removing cyanobacterial toxins in water by using visible radiation [37, 66]. Castillo-Ledezma et al. have recently demonstrated the capability of N–F–TiO<sub>2</sub> 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–TiO<sub>2</sub> process possesses higher efficiency than the regular TiO<sub>2</sub> and solar disinfection processes [2]. Similar results were found by Wong et al. for nitrogen-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> in photoreactors where the semiconductor is recovered after the treatment. According to various lab-scale research reports [14], the use of TiO<sub>2</sub> 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].

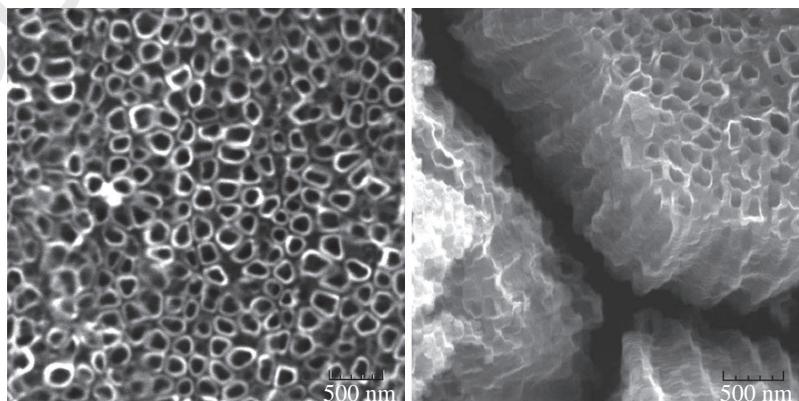
Several supporting materials, from sand to quartz optical fiber, have been reported so far for TiO<sub>2</sub> immobilization. During the past few years, the in situ generation of catalysts seems to be the most promising technology for catalyst immobilization [71]. Other authors [72] have demonstrated 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 TiO<sub>2</sub> PARTICLES AND NANOTUBES

Nanostructured TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>, including their PC activity and PV response [76].

One of the most promising TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 μm (Fig. 2.2).

The highly ordered structure can improve the transport of photogenerated electrons in the TiO<sub>2</sub> 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  $2 \times 10^{-4}$  M [80].

Also, in electrocatalysis,  $\text{TiO}_2$  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,  $\text{TiO}_2$  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  $\text{TiO}_2$  film. Gold as well as other noble metals like silver, palladium, platinum, and ruthenium have been deposited on TDNs in order to enhance  $\text{TiO}_2$  PC properties [81].

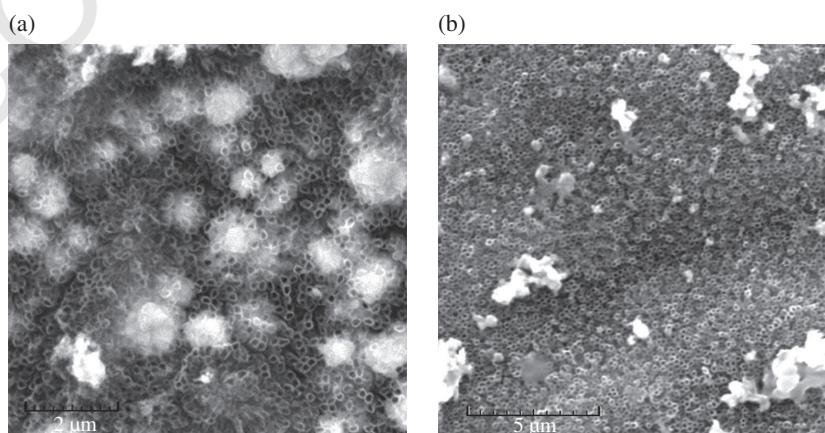
## 2.7 PHOTOCATALYSIS ON $\text{TiO}_2$ NANOTUBES

In recent years colloidal and particulated  $\text{TiO}_2$  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  $\text{TiO}_2$  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,  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$ /electrolyte interface [82]. Photocatalysis can be improved if two metals are simultaneously used to modify  $\text{TiO}_2$  as it was investigated for a Au–Pd–co-modified  $\text{TiO}_2$  nanotube film (Au–Pd– $\text{TiO}_2$ ). The activities of naked  $\text{TiO}_2$  and Au–Pd– $\text{TiO}_2$  toward malathion degradation were compared. The study showed that 73.8% of malathion was removed in the presence of naked  $\text{TiO}_2$ , but 98.2% malathion removal was achieved when Au–Pd– $\text{TiO}_2$  was used instead of naked  $\text{TiO}_2$  [83].

As we can see, one of the major trends in the environmental use of  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{PbO}_2$  (Fig. 2.3a) or  $\text{SnO}_2$  doped with Sb (Fig. 2.3b) [85–87].

$\text{PbO}_2$  and  $\text{SnO}_2$  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)  $\text{PbO}_2$  deposited on TDN; (b) Sb– $\text{SnO}_2$  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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 SnO<sub>2</sub>, SiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, and CdS [87, 91, 92]. Thus, for example, a photocatalyst like Bi<sub>2</sub>O<sub>3</sub> that is capable of oxidizing water under a visible light irradiation could be loaded onto a TiO<sub>2</sub> nanotube array electrode, and the composite electrode achieved higher catalytic activities toward 2,4-dichlorophenol degradation than the individual Bi<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, where Bi<sub>2</sub>O<sub>3</sub> is photoactive under visible light and TiO<sub>2</sub> 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 TiO<sub>2</sub> electrode for *E. coli* inactivation. High surface TiO<sub>2</sub> nanotubes resulted in high photocurrent and an extremely rapid *E. coli* inactivation rate (~10<sup>6</sup> CFU mL<sup>-1</sup> killed in less than 10 min). Recently, a Ag/AgBr/TiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>) 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<sub>2</sub>O<sub>3</sub> had higher toxicity at the same concentration [107, 108].

Copper (II) oxide (CuO) and copper (I) oxide (Cu<sub>2</sub>O) 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 50nm 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<sub>2</sub>O 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 pneumoniae*, *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<sub>2</sub>) 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<sub>2</sub>, bulk CeO<sub>2</sub> showed less toxicity than their nanosized counterparts [126].

Nitrogen-doped ZrO<sub>2</sub> has been reported to effectively inhibit the growth of *E. coli* and biofilm heterotrophic bacteria under solar light illumination [68]. Iron oxides (FeO, α-Fe<sub>2</sub>O<sub>3</sub>, β-Fe<sub>2</sub>O<sub>3</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) 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<sub>2</sub>, 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<sub>3</sub>O<sub>4</sub> 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.

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