

Chapter 8

Ecotoxic Effect of Photocatalytic Active Nanoparticles on Human Health and the Environment



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8.1 Introduction

Nanotechnology is a rapidly expanding industry that covers many areas of science and technological utilization. This technology has already yielded a variety of commercial products such as cosmetics, medical science equipment, self-cleaning windows, paints, and stain-resistant clothing. For personal care products, some nanoparticles (NPs) such as zinc oxide (ZnO) and titanium dioxide (TiO₂) are applied in toothpaste, sunscreens, and beauty products (Serpone et al. 2007). Similarly, Ag NPs are used as antimicrobial additives in food packaging, detergents, and textiles such as socks and underclothes (Maynard and Michelson 2006). The integration of nanomaterials in the life of consumers has caused increased concern regarding hazards to the environment and to human health. Accidental exposure to the nanoparticles may arise at three stages: (1) during production of NPs, (2) via release from the solar/coatings/batteries or during separation of the material, and (3) after recycling/disposal.

Discussions are suggested by warnings and complaints from researchers and toxicologists that arise from the challenges correlated with the toxicity evaluation of nanomaterials. When the whole environment is concerned, the issue is more intricate. Although there was formerly a considerable amount of toxicological information concerning available NPs (obtained at different biological levels), ecotoxicological data on nanoparticles are just emerging (Kahru and Dubourguier 2010).

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However, there is a considerable amount of experience and data on environmental risk evaluation of chemicals. The main properties of NPs, such as high specific surface area, large reactive sites on the surface that cause an extensive fraction of atoms to be located on the external rather than in the internal of NPs, and also their mobility, can cause unexpected health or environmental risks (Maynard et al. 2006; Wiesner et al. 2006; Prasad et al. 2016). Accordingly, organisms, and particularly those that interact with their environment such as aquatic plants and algae, are expected to be affected as a consequence of their exposure to nanoparticles.

In this chapter, the environmental treatment and ecotoxicity of nanoparticles to organisms such as algae and aquatic plants are investigated. First, the behavior of NPs in aquatic systems as the basic living place for algae and plants are discussed, and then the toxicity of NPs is examined.

8.2 Photocatalytic Nanomaterial

Photocatalytic nanoparticles have an important function to apply an impressive photocatalytic reaction, and therefore it is important that we select them carefully to carry out both acceptable energy of light and proper electronic structure for its photoactivation (Ohtani 2013). Photocatalysis semiconductor NPs accomplish the requirements of photocatalysts, and the bandgaps are used to explain their electronic structure, which is characterized by the valence band (VB) and the conduction band (CB), which is located on top of the valence band and separated from it by an energy gap, named the bandgap (E_g) (Hernández-Ramírez and Medina-Ramírez 2015). Photocatalytic process are based on electronic excitation of the catalyst (semiconductor) by UV light irradiation. By this excitation of semiconductor with energy from photons, and equal or higher energy bandgap of semiconductor, the electron is promoted from VB of semiconductor to CB, thus leaving a positive hole (h^+) on the VB. The promoted electrons and holes migrate to the surface of the photocatalyst and the oxidation-reduction process, respectively, occurs (Fig. 8.1) (Pichat 2007).

Semiconductors are also classified as binary and ternary compounds; however, the appropriate semiconductors for photocatalysts must achieve the following: have an appropriate bandgap energy (1–4 eV), high stability, and an appropriate band edge place that matches the intended use radiation absorption and nontoxicity (Hernández-Ramírez and Medina-Ramírez 2015). The usual classes of photocatalytic nanoparticles are illustrated in Fig. 8.2.

Most photocatalytic NPs and composites are metal oxides. Such binary oxides as titanium dioxide (TiO_2), tungsten oxide (WO_3), zinc oxide (ZnO), and iron oxide (Fe_2O_3) are the most studied semiconductors in photocatalytic experiments. TiO_2 is mostly used in different technical applications because of its hydrophilicity, stability, high reactivity, and low cost (Schneider et al. 2014). The best known polymorphs of TiO_2 NPs are rutile, anatase, and brookite with bandgap energies of 3.02, 3.20, and 2.96, respectively (Gupta and Tripathi 2011). The anatase phase displays

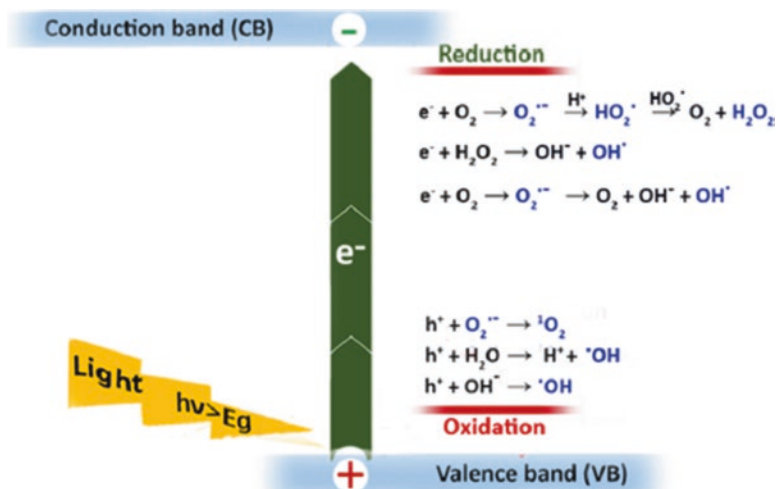


Fig. 8.1 The mechanism of reactive oxygen species (ROS) generation

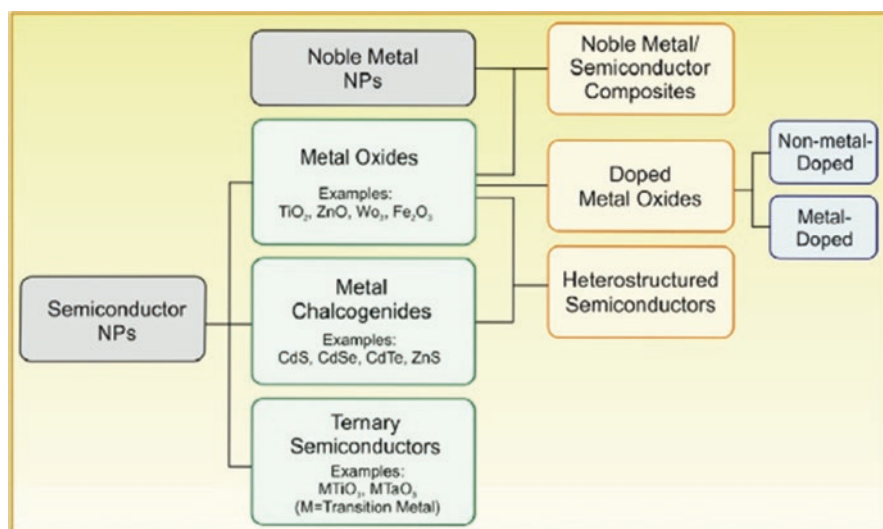


Fig. 8.2 Classes of photocatalytic nanoparticles (NPs) and their composites. (From Friehs et al. 2016)

the highest photocatalytic performance and thus it is applied in photocatalytic processes. The rutile phase is applied as a thickener and pigment in cosmetic products and other uses for its UV light-absorbing properties (Mueller and Nowack 2008). Hence, brookite and anatase are used in dye-sensitized solar cells (Jiang et al. 2002). Such characteristics have led to the use of TiO_2 NPs for different applications, such as light-emitting diodes, self-cleaning surface coatings, disinfectant sprays, solar

cells, water treatment agents, and topical sunscreens (EPA 2009). However, TiO₂ NPs have many different sources. Degussa P25 is known as the standard nanoparticle in the field of photocatalysts as its well-defined nature consists of rutile and anatase phases in a ratio of 1:3 (Friehs et al. 2016). TiO₂ NPs are applied in sunscreen cosmetics as an UV absorbent. To decrease its photo-reactivity, nano silica and other compounds can be added to TiO₂ NPs as a surface coating; hence, TiO₂ NPs can protect human skin and plastics from UV irradiation (EPA 2009). ZnO nanoparticles provide good catalytic and photochemical properties; hence, it is considered as the most applicable photocatalytic semiconductor after TiO₂ (Hatamie et al. 2015). Because of its high quantum efficiency, ZnO is usually preferred in comparison to TiO₂ to degrade and decompose organic contaminants (Farbod and Jafarpour 2012). The main disadvantages of ZnO NPs are the possibility of the photo-corrosion phenomenon at low pH values (Di Paola et al. 2012). The bandgap energy of the ZnO semiconductor is 3.37 eV, with a wide excitation binding energy (60 eV), and presents near-UV light irradiation, piezoelectricity, that is more attractive in electronic sensor and transparent conductivity. ZnO NPs are extensively used in products such as foods (source of Zn nutrient), ceramics, plastics, cement, glass, rubber, fire retardants, paints, lubricants, pigments, and batteries. Moreover, ZnO nanoparticles have been used in personal care products such as cosmetics and sunscreens because of their superior UV absorption and reflective characteristics. The production of nanoparticles for only sunscreen cosmetic products was estimated to be about 1000 tons between 2003 and 2004, consisting of ZnO and TiO₂ NPs (Borm et al. 2006).

8.3 Nanoparticles as Potential Aquatic Contaminants

Industrial wastes and products tend to be released to the aquatic environment, such as rivers, estuaries, drainage ditches, lakes, and coastal waters, despite protections. Accordingly, as the nanoproductions industries start large-scale production, it is certain that nanoscale products will be discharged into surface waters. Thus, a crucial issue is that we have beneficial risk assessment procedures in place in the fastest possible time to handle potential hazards.

Current studies indicate that the concentration of ZnO NPs in the UK environment range from less than 100 µg/l in water to a few milligrams per kilogram (mg/kg) in soil (Boxall et al. 2007); as well, a further study by Gottschalk confirmed ZnO NPs concentration as about 10 ng/l in natural waterways and 430 ng/l in wastewater in Europe (Gottschalk et al. 2009) (Table 8.1).

Moreover, studies observe that the metallic Ti concentrations found in the surface water are about 600 mg/l (Kägi et al. 2008). Kiser et al. (2009) estimated the levels of Ti nanomaterial release from wastewater plants: raw sewage contains 100–3000 mg/l of Ti. Ti concentrations in wastewater effluents ranged from <5 to 15 mg/l. Two studies modelled the TiO₂ NPs discharged into the environment (Gottschalk et al. 2009; Mueller and Nowack 2008); the estimated environmental

Table 8.1 Modeled concentrations of TiO₂ and ZnO nanoparticles (NPs) released into environmental compartments in different countries, shown as mode (most frequent value) and as range of the lower and upper quantiles (Q_{0.15} and Q_{0.85})

Environmental compartment	Predicted environmental concentration, mode (Q _{0.15} , Q _{0.85}) ^a (mg/l, mg/m ³ , or mg/kg)		
	Switzerland	Europe	U.S.
<i>TiO₂ NP</i>			
Surface water	0.021 (0.016, 0.085)	0.015 (0.012, 0.057)	0.002 (0.002, 0.010)
STP effluent	4.28 (3.50, 16.3)	3.47 (2.50, 10.8)	1.75 (1.37, 6.70)
STP sludge	211 (172, 802)	136 (100, 433)	137 (107, 523)
Sediment	499 (426, 2382)	358 (273, 1409)	53 (44, 251)
Soil	0.28 (0.21, 1.04)	1.28 (1.01, 4.45)	0.53 (0.43, 2.13)
Sludge-treated soil		89.2 (70.6, 310)	42.0 (34.5, 170)
Air	0.001 (0.0007, 0.003)	<0.0005	<0.0005
<i>ZnO NP</i>			
Surface water	0.013 (0.011, 0.058)	0.010 (0.008, 0.055)	0.001 (0.001, 0.003)
STP effluent	0.441 (0.343, 1.32)	0.432 (0.340, 1.42)	0.3 (0.22, 0.74)
STP sludge	21.4 (16.8, 64.7)	17.1 (13.6, 57.0)	23.2 (17.4, 57.7)
Sediment	3.33 (3.30, 56.0)	2.90 (2.65, 51.7)	0.51 (0.49, 8.36)
Soil	0.032 (0.026, 0.127)	0.093 (0.085, 0.661)	0.050 (0.041, 0.274)
Sludge-treated soil		3.25 (2.98, 23.1)	1.99 (1.62, 10.9)
Air	<0.0005	<0.0005	<0.0005

From Gottschalk et al. (2009)

^aFor surface water, air, and sewage treatment plant (STP) effluents, the results obtained are current 2008 nanoparticles concentrations; for soil, sludge-treated soil, and sediments, the annual increase of engineered nanoparticle (ENM) concentration

concentrations are exhibited in Table 8.1. The estimated concentrations of TiO₂ NPs in consumer products were 1030 mg/kg for soil and 24.5 mg/l for water (Boxall et al. 2007). It is predicted that once nanoparticles are in the water, they will most likely agglomerate and partition to suspended particulate matter and sediment (Boxall et al. 2007). Agglomerated particles are usually less mobile and may interact with sediment-dwelling organisms and filter feeders (Farré et al. 2009; Menard et al. 2011). Humic acids have been noted to have considerable influence on the agglomeration of TiO₂ NPs (Pettibone et al. 2008). Many studies have already described the effects of ZnO and TiO₂ NPs on biological systems. TiO₂ and ZnO NPs have been shown to generate reactive oxygen species (ROS) in the absence and presence of UV radiation (Armelaio et al. 2007; Reeves et al. 2008). The accurate mechanisms of toxicity of ZnO, TiO₂, and other metal NPs are generally unknown (Griffitt et al. 2008), but recent studies have presented that the toxicity of NPs is essentially influenced by properties such as shape and morphology, particle size, and surface properties (Crane et al. 2008). There is emerging knowledge on the ecotoxicity of ZnO and TiO₂ NPs, with many studies related to aquatic organisms, algae, fish, and freshwater invertebrates. Recently, invertebrates, algae, and fish species were tested: freshwater invertebrates are the most studied group for which the

most data exists, and after that algae and then freshwater fish. Similar data among these groups of organisms were also obtained for other NPs (Cattaneo et al. 2009). As there is a lack of available knowledge on the toxic effects of TiO_2 and ZnO NPs on sedimentary, terrestrial, and aquatic plants, research in the field is needed.

8.4 Bioavailability of Nanoparticles in Different Environments

Ecotoxicological tests are tools applied within ecological hazard assessment frameworks to understand the aquatic toxicology and intrinsic dangers of chemical compounds that leach into the environment. The term ecotoxicity was mainly developed for water-soluble chemical substances and aquatic test organisms. However, in spite of the apparent path of exposure and the mechanisms of ecotoxicity, bioavailability exists as a key factor for the hazard assessment of synthetic nanoparticles. Bioavailability is a dynamic intention that evaluates the physical, chemical, and biological processes of exposure. Bioavailability combines concepts of ecotoxicology and environmental chemistry, incorporating concentration of contaminant and an organism's treatment in the given environment. Bioavailability of nanoparticles depends on the physicochemical characteristics of the particles (solubility and aggregation) and behavior of nanoparticle–organism in the particular environment. Hence, environmental hazard assessment of NPs needs characterization of NPs in entire processes of exposure.

8.5 Ecotoxicity of Nanoparticles

8.5.1 *Entry of Nanoparticles into Algae, Aquatic Plants, and Fungi*

Apart from the animals, most cells of algae, plants, and fungi contain cell walls that form a primary site which acts as a barrier for the entry of NPs into their cells. The majority of cell wall components are proteins and carbohydrates that are connected to form a hard complex network (Knox 1995). The functional groups, such as phosphate, carboxylate, amine, imidazole, hydroxyls, and sulfhydryl are included in these biomolecules (Vinopal et al. 2007). Cell walls in algae and plants mostly consist of cellulose. Moreover, algae have polysaccharides and glycoproteins in their cell walls. The semipermeable properties of cell walls can permit small molecules to cross cell walls, whereas for larger molecules they are limited. The pore diameter of cell walls ranges from 5 to 20 nm (Fleischer et al. 1999; Zemke-White et al. 2000). Thus, only NPs with a diameter smaller than the pore size are expected to cross through the cell wall. Moreover, the interactions of the cells with NPs might

influence the pores of the cell wall and form a new pore size that might be larger than usual and hence allow increased entry of NPs through the cell wall and after that to conjoin the plasma membrane. Currently, the entry routes of nanoparticles through this lipid membrane have been debated (Moore 2006). In the endocytic process, the plasma membrane generates a hole structure that surrounds the NP and moves it into the cell. The NPs might pass the cell membranes using blended transport carrier proteins. Upon the entry of the NP into the cell, they may attach to organelles such as the endoplasmic reticulum, the endolysosomal system, and Golgi apparatus and then hamper those metabolic processes. Moreover, at high concentrations of NPs, the nucleus of macrophage cells may display degeneration, rarefaction, and enlargement (Jia et al. 2005).

8.5.2 Effects of Nanoparticles on Algae and Aquatic Plants

Although there is little information on the effects of NPs on algae and plants, both direct and indirect effects have been found. Direct ecotoxic effects of nanoparticles on organisms are mainly obtained by their particle size, surface reactivity, and chemical composition. Some ecotoxicological effects of TiO₂ NPs on algae have been obtained in recent years (Kahru and Dubourguier 2010; Klaine et al. 2008). Ecotoxicity tests for algae have been evaluated with three species: *Desmodesmus subspicatus*, *Pseudokirchneriella subcapitata*, and *Chlamydomonas reinhardtii*. Growth inhibition was usually measured after 72 h (Aruoja et al. 2009; Blaise et al. 2008; Hund-Rinke and Simon 2006) or 96 h (Griffitt et al. 2008), and different 72-h EC₅₀ values were studied for TiO₂ NPs. For example, in *P. subcapitata*, values ranged from 5.83 mg/l of Ti (Aruoja et al. 2009) to 241 mg/l of TiO₂ (Hartmann et al. 2010). The 72-h EC₅₀ of TiO₂ assessed for *D. subspicatus* was 32 mg/l (mainly anatase, particle size of 25 nm), but when another TiO₂ form (100% anatase, particle size of 100 nm) was measured, there was no effect at ranges less than 50 mg/l of TiO₂ (Hund-Rinke and Simon 2006). Acutely variable LC₅₀ and 72-h EC₅₀ values were measured for TiO₂ NPs tested with *P. subcapitata* (Table 8.2). No clear correlations between the particle size and effects on algae *P. subcapitata* could be recognized. For example, nanoparticles described at levels below 100 nm in diameter were not totally toxic to these algae (Blaise et al. 2008), whereas sonicated nanoparticles with sizes between 25 and 70 nm in diameter were much more toxic (Aruoja et al. 2009). On the other hand, evidence indicated that the toxicity of two sizes (<10 nm and 30 nm) of TiO₂ NPs did not cause much difference, and thus no clear dependence between the particle size and effects was observed (Hartmann et al. 2010).

A relationship between the nanoparticle-specific surface area and effect concentrations is shown in Fig. 8.3a. With increasing specific surface area, the toxicity of TiO₂ NPs to the alga *P. subcapitata* decreases. For example, the particles with a specific surface area of 288 m²/g are less toxic to *P. subcapitata* than the particles with a specific surface area of 5.8 m²/g. Moreover, as shown in Fig. 8.4 and Table 8.3,

Table 8.2 Physicochemical properties of TiO₂ NPs and toxicity values for the alga *Pseudokirchneriella subcapitata*

Species	Particle size (nm) ^a	Crystal phase	BET (m ² /g) ^b	DLS (nm) ^c	Toxicity value (mg/l)
<i>P. subcapitata</i>	/	w99% TiO ₂ core with 1% Al surface coating	5.8	380	EC ₅₀ = 16 (12–22) (conc. not measured) EC ₅₀ = 61 (52–72) (nominal conc.)
	/	79% rutile/21% anatase; 90 wt% TiO ₂ , 7% alumina, 1% amorphous silica	38.5	140	EC ₅₀ = 21 (16–26) (conc. not measured) EC ₅₀ = 87 (83–91) (nominal conc.)
	<10	67.2% anatase/32.8% amorphous	288	1261	EC ₅₀ = 241 (95.6–609)
	25–70	/	/	/	EC ₅₀ = 5.83 (3.75–7.58)
	30	72.6% anatase/18.4% rutile/9% amorphous	47	416	EC ₅₀ = 71.1 (59.4–85.1)
	<100	99.9% TiO ₂	/	/	IC ₂₅ > 100

From Menard et al. (2011)

/ no data available, EC₅₀ median effective concentration, IC₂₅ 25% inhibition concentration, () = 95% confidence intervals

^aParticle size reported by the manufacturer

^bSpecific surface area calculated with Brunauer, Emmett, and Teller method (BET)

^cMedian values for particle size in media determined with dynamic light scattering (DLS)

the larger surface area per mass, compared with greater particle sizes of the same component, presents NPs as more reactive biologically (Oberdörster et al. 2005). The smaller particle sizes show an apparent concentration–effect relationship, whereas the larger sizes cause less toxicity (Hund-Rinke and Simon 2006). On the other hand (Fig. 8.3b), the effect concentrations could not be connected to the median values of the size of nanoparticles in media (Warheit et al. 2007). The 140 nm size of nanoparticles and 380 nm in particle diameter in media have the same toxicities to the alga *P. subcapitata* with 72-h EC₅₀ of 21 mg/l and 16 mg/l, respectively. Nanoparticles 380 nm in size in media are more toxic than those 1261 nm to the alga *P. subcapitata* (Fig. 8.3b). As well, there is no correlation between the crystalline form of nanoparticles applied in the studies and toxicity for algae (Table 8.2). Studies by some researchers in which particles with the same sizes were tested with the three species of algae observed that the sensitivity to TiO₂ for the alga *P. subcapitata* is more than for *C. reinhardtii*, and *D. subspicatus* is the least sensitive (Aruoja et al. 2009; Hund-Rinke and Simon 2006), although given that some of the variable 72-h EC₅₀ values that were obtained for *P. subcapitata* are very high, this cannot be confirmed. It might be possible to evaluate species-specific sensitivity to TiO₂ NPs after more data are acquired on all species with NPs prepared similarly.

No measurements of agglomeration size, which could possibly affect inhibitory impressions, were reported. Effects of Zn and ZnO NPs on metabolic growth in

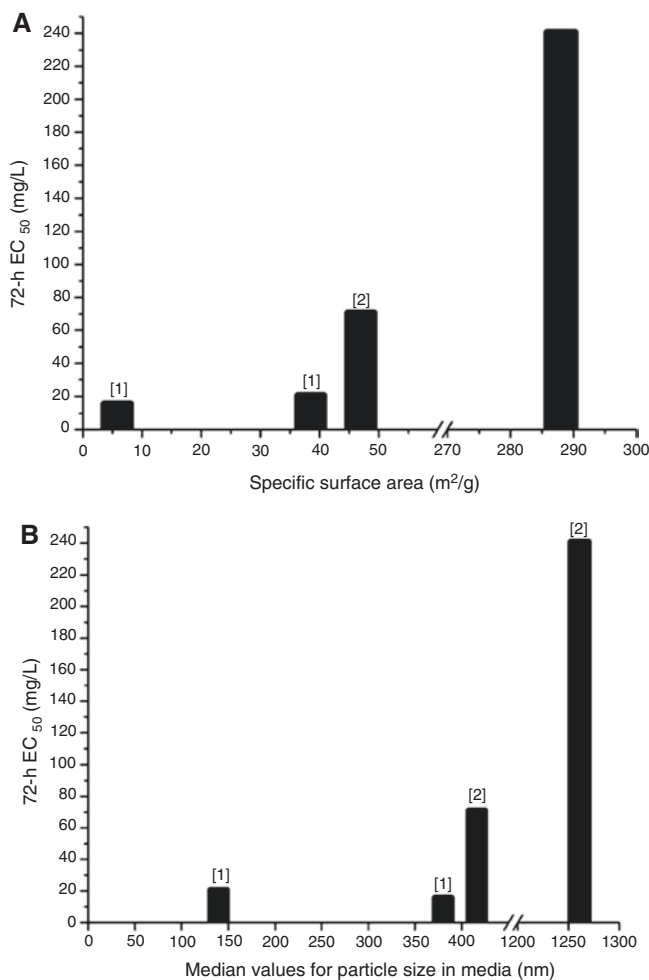


Fig. 8.3 Relationship between (a) specific surface area (measured with BET and 72-h EC₅₀ values, and (b) median values for particle size in media (evaluated with DLS) for TiO₂ NPs for the alga *Pseudokirchneriella subcapitata*. (References: [1] Warheit et al. 2007; [2] Hartmann et al. 2010; Menard et al. 2011)

radish and ryegrass have been shown to be related to their particle size more than their chemical composition (Lin and Xing 2007). At the same time, Al₂O₃ was shown to affect root growth (Yang and Watts 2005). Moreover, silver (Ag) NPs may motivate membrane conversions, increment membrane porosity, and in bacteria cells disrupt their capacity to control transport through the membrane (Pal et al. 2007; Sondi and Salopek-Sondi 2004). Increasing membrane porosity also facilitates the entrance of NPs into cells (Morones et al. 2005). Similarly, it is clear that the properties of materials for nanoparticles differ considerably from bulk materials of the same composition because the increased specific surface area and reactivity

Fig. 8.4 Relation between specific surface area ($\text{m}^2 \text{kg}^{-1}$) of a spherical nanoparticle and particle size (diameter in nm) with a density of 1000 kg m^{-3} (Navarro et al. 2008)

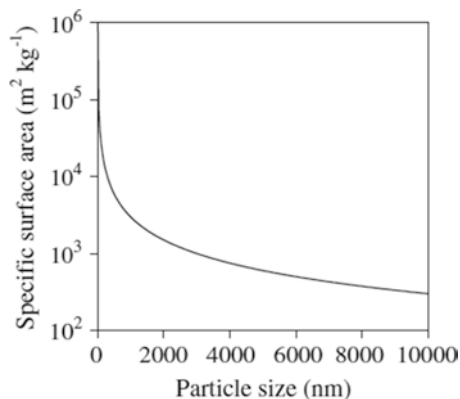


Table 8.3 The most studied nanoparticles (NPs) and their physicochemical properties

Type	Diameter (nm)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
Fullerene (C_{60})	0.72	~10,000
Silver (Ag)	10	9–11
Titanium oxide (TiO_2)	5	200–220
Zinc oxide (ZnO)	20	~50
Copper oxide (CuO)	30–50	~13.1
Iron oxide (Fe_2O_3)	20–50	~50
Quantum dots	1–10	100–1000
Single-walled carbon nanotubes	1–2 (diameter) 5–30 μm (length)	~400
Multi-walled carbon nanotubes	<8 (OD) ^a 2–5 (ID) ^a 10–30 μm (length)	~500

From Navarro et al. (2008)

^aOD outside diameter, ID inside diameter

may cause increased bioavailability and toxicity (Nel et al. 2006). Indeed, CuO NPs were as much as 50 times more toxic than bulk CuO particles towards algae (Aruoja et al. 2009), crustaceans (Heinlaan et al. 2008), yeast (Kasemets et al. 2009), and protozoa (Mortimer et al. 2010). As well, the antibacterial effects of silver NPs are dependent not only on size (Morones et al. 2005) but also on shape (Pal et al. 2007). The inhibitory effects of Ag NPs to nitrifying organisms are correlated with the sizes in fractions less than 5 nm, which were rather more toxic towards bacteria than their bulk species (Choi and Hu 2008). The indirect effects of NPs are caused mostly by release of toxic ions, for example, metal NPs or the generation of ROS. Furthermore, NPs themselves may act as pollutant carriers, hence enhance or reduce the bioavailability of other toxic matters (Fig. 8.5). Some components present in the environmental matrix might increment NP stability (OM) and thus

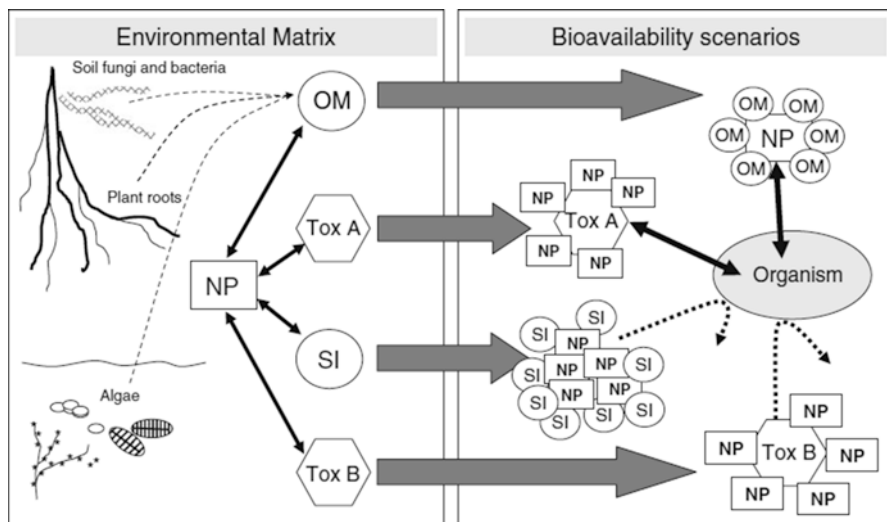


Fig. 8.5 Nanoparticles interactions with toxicants (Tox A and B), salt ions (SI) and organic matters (OM) released by bacteria, plants, algae, and fungi (From Navarro et al. 2008)

bioavailability, whereas others (SI) might cause the aggregation of NPs, hence reducing their bioavailability (rejected organisms are shown as dotted arrows in Fig. 8.5) (Navarro et al. 2008).

As an example of physical abatement, the deposition of NPs on the surface of photosynthetic organisms may prevent photosynthetic activity from shading effects by reducing light availability, and also because of NP toxicity (Fig. 8.6) (Navarro et al. 2008).

As a function of the trend to agglomerate and correlate with other organic matters (Chen and Elimelech 2007), sorption of NPs to algal cells is expected. For example, results show that TiO_2 NPs were adsorbed onto the surface of the algal cell, at a 2.3-fold increment of cellular weight (Huang et al. 2005). Similarly, by aggregation of carbon black, which bound to sperm cells, fertilization success was reduced on *Fucus serratus* (a marine seaweed) (Fernandes et al. 2007). Sorption of greater nanoparticle aggregates to cell walls may also adjust the cellular adsorption of essential nutrients through plugging of the walls or nutrient sorption. In addition, organisms may excrete suspensions as a feedback reaction to alter the NP toxicity. Metal chelate exudation from root systems, for example, siderophores, may decrease the bioavailability of toxic metal ions released from metallic NPs by complexation (Fig. 8.5). Such components may also suppress the dissolution rate of metal from metal oxide NPs or from metallic NPs. Simultaneously, algae can generate substances that may induce metal ion chelation or NP flocculation and cause the bioavailability of both nanoparticle and metal ions thus released to decline (Soldo et al. 2005). Results showed that exopolymeric material production can cause increase in algae at exposure to NPs and may thus cooperate to detoxification reactions (Miao

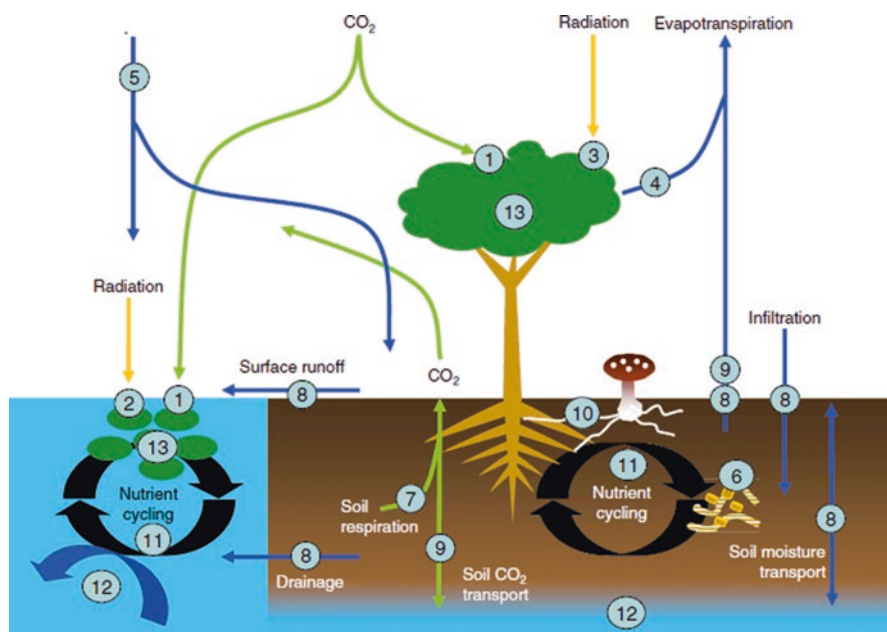


Fig. 8.6 schematic diagram of some aquatic ecosystem processes. Nanoparticles impacts on photosynthetic organisms may decrement the fixation of CO_2 (1); NPs adsorbed (2) or deposited (3) on active surfaces might reduce gas exchange or light availability (4) and hence photosynthesis; NPs in the atmosphere might increase the nuclei available for raindrop formation (5), thus cause to precipitation; NPs' effects on fungi and bacteria(6) might influence on soil respiration (7), and other soil-texture-associated processes such as transport of liquids (8) or gases (9), also modifying symbiotic relationships (10). As well, this might lead to damages in nutrient cycling (11), water purification (12), and biomass production (13). (From Navarro et al. 2008)

et al. 2007). Figure 8.5 shows that bioavailability of NPs can be both improved (Terashima and Nagao 2007) and decreased (Dunphy Guzman et al. 2006) by the abiotic characteristics of the surrounding matrix.

8.6 Generation of Oxidative Stress

Oxidative destruction, caused by either internalized or extracellular NPs, has been discussed as one of the main reasons for nanoparticle toxicity (Nel et al. 2006). Nanoparticles might generate reactive oxidant species (ROS) towards their interaction with organisms or by some agents such as UV radiation that is present in the environment. ROS formation is exactly related to NPs with photocatalytic characteristics such as TiO_2 (Kus et al. 2006). ROS-induced oxidative stress caused some physiological effects at all levels of biological formation. Thus, destructive effects of TiO_2 NPs on bacteria have been improved by sunlight or UV irradiation (Adams

et al. 2006). Other NPs, such as fullerenes and silver NPs, also showed the ability to generate ROS by UV exposure (Rodríguez-Moya et al. 2007). Under usual conditions, ROS-induced destruction is adapted by the cellular antioxidant cascade: glutathione peroxidase, catalases, enzymes such as superoxide dismutase (SOD), and non-enzymatic antioxidants, for example, ascorbic acid, α -tocopherol, and glutathione (Blokhina et al. 2003). Currently, Von Moos and Slaveykova (2014) considered various inorganic NPs such as CuO, ZnO, and Ag NPs that induced oxidative stress in aquatic environments. The cellular mechanisms based on oxidative stress and ROS production induced by nanoparticles in aquatic microorganisms and the methods for the evaluation of oxidative stress and ROS have been comprehensively discussed by von Moos and Slaveykova (2014).

8.6.1 Oxidative Stress-Related Effects of Nanoparticles on Relevant Organisms

For evaluation of the NP potential to apply oxidative stress to different environmentally relevant organisms, some biomarkers, such as catalase (CAT), increased activities of SOD, glutathione peroxidase (GPx), increased levels of metallothionein-like proteins and glutathione-S-transferase (GST) and have been investigated. There are many examples representing ROS as one of the primary drivers of silver NPs toxic effects. Yet, toxicity of NPs may be mostly the result of their toxicants release (Brunner et al. 2006; Navarro et al. 2008). Ag^+ released from a silver (Ag) NP may inhibit respiratory enzymes and cause induced oxidative stress upon ROS generation (Kim et al. 2007; Aziz et al. 2014, 2015, 2016, 2019). Ag^+ may also link to phosphorus- and sulfur-containing molecules (taurine, *S*-adenosylmethionine, glutathione, cysteine, etc.) involved in cell antioxidant protection (Pappa et al. 2007; Prasad and Swamy 2013), and may result in the reduction of the intracellular concentration of molecules (Hussain et al. 2005). Hence, Ag NPs were found to decrease photosystem II quantum yield, cell-specific growth rate, and chlorophyll *a* capacity of the marine phytoplankton *Thalassiosira weissflogii* and the toxic factors were calculated by the release of Ag^+ (Miao et al. 2007). Similarly, results obtained by Navarro et al. (2007) demonstrated that toxicity of Ag NPs to the photosystem II quantum yield of the freshwater alga *Chlamydomonas reinhardtii* also correlated to the release of Ag^+ . Both studies indicate that about 1% of the Ag NPs was released as ionic silver (Ag^+). Moreover, concentrations of Ag^+ were too low to clear the toxicity exhibited by Ag NPs, so recommended the significance of the Ag NP–cell interaction (Navarro et al. 2007; Sotiriou and Pratsinis 2010; Yang et al. 2011). Moreover, by comparing the toxicity of ZnO NPs with that of Zn^{2+} , it was demonstrated that ZnO NP toxicity may depend on the solubility of the NPs (Franklin et al. 2007). Based on recent knowledge, CuO NPs tend to exert more oxidative destruction than Ag NPs. As for Ag NPs, the context of participation of CuO NPs and the dissolved Cu ions to the generation of ROS is still debatable. It is clear that ions of redox-active metals such as Cu may transfer free radicals by the Fenton reaction and

deliver intracellular oxidative stress (Valko et al. 2005). The reduction mechanism of cuprous ion [Cu(I)] to cupric ion [Cu(II)] in the presence of biological reducing agents including glutathione (GSH) or ascorbic acid is shown in the following reaction. In this reaction, reactive hydroxyl radicals (OH^\bullet) are produced from hydrogen peroxide (H_2O_2) by the Fenton reaction.



Induction of ROS by CuO NPs has been presented at different levels of biological constitution. Luminescent bacterial tests have demonstrated ROS-producing potential of aqueous compounds of CuO NPs in recombinant *E. coli* strains (Ivask et al. 2010). Currently, results show that oxidative stress was induced by CuO NPs and DNA damage protection systems in recombinant *E. coli* strains at very low toxic concentrations (0.1 mg Cu/l) (Bondarenko et al. 2012), although these effects were most probably provoked by dissolved Cu ions. Applerot et al. (2012) indicated that upon connection to bacteria, lipid peroxidation and intracellular oxidative stress are induced by CuO NPs. Mortimer et al. (2010) described the effects of CuO NPs on membrane lipids for the unicellular protozoa *Tetrahymena thermophila*: in reaction to exposure to CuO nanoparticles (80 mg/l), the protozoa altered membrane fatty acid suspensions to more hardness by increasing the content of saturated fatty acids (C18:0 and C16:0) and decreasing the content of unsaturated fatty acids (C18:3 *cis*-6,9,12 and C18:2 *cis*-9,12). Peroxidation of lipid caused by CuO nanoparticles has also been discussed in the bacteria *E. coli* and *Bacillus subtilis* (Applerot et al. 2012), the tissue and gills of rainbow trout (Shaw et al. 2012), and the green alga *C. reinhardtii* (Cheloni and Slaveykova 2013). ZnO is a photocatalytic nanoparticle that can promote ROS production equal to or more than its bandgap energy (3.37 eV) that correlates to 368 nm light (Ma et al. 2013). In fact, studies by Yu et al. (2011) and Xiong et al. (2011) demonstrated that under irradiation, at concentrations more than 10 mg/l, ZnO NP components induced hydroxyl radicals (OH^\bullet). Simultaneously, no hydroxyl radical generation was obtained in bulk ZnO particles. Antibacterial properties of ZnO NPs to different bacterial species (Applerot et al. 2009) and yeast (Lipovsky et al. 2011) were generated by reaction of the ZnO NP surface with H_2O_2 , which generates hydroxyl radicals (OH^\bullet). H_2O_2 production was also indicated as one of the main factors participating in the antibacterial activity of ZnO NPs to *E. coli* (Sawai et al. 1998). Particle-induced ROS generation can result in a range of biological reactions, depending on the type of cellular pathways that are activated by oxidative stress and the relative abundance of ROS formation (Xia et al. 2008). Excessive formation of these ROS species can lead to cell membrane damage, which may result in cell lysis and finally cell death (Zhang et al. 2007) or facilitate aggregation and internalization of the NPs into cells, leading to toxicity (Xie et al. 2011). An investigation with the bacteria *Pseudomonas chlororaphis* indicated that ZnO NPs might induce intracellular ROS without illumination (Dimkpa et al. 2011). ROS protection systems have been shown to contribute in the ZnO toxicity reaction of bacteria. Lipid peroxidation caused by ZnO NP-induced ROS has been demonstrated in several organisms such as earthworms (Hu et al. 2010), bacteria (Kumar

et al. 2011), and fish (Xiong et al. 2011). By increasing in lipid peroxidation levels because of exposure to ZnO, NPs might represent that the self-scavenging content of antioxidant defense systems was increased (Hao and Chen 2012).

8.7 Photo-Induced Toxicity

A special case of ecotoxicity is given for nanomaterials that have a photocatalytic properties. Ecotoxic effects of these particles might differ from dark and light conditions. For example, the EC_{50} assessed by incubation with TiO_2 for *E. coli* declined from 583 mg/l to 1.68 mg/l when irradiated with sunlight for 30 min (Dasari et al. 2013). An ecotoxic effect of TiO_2 particles as a photocatalytic material has been explained for various organisms, such as bacteria (Dalai et al. 2012), algae (Lee and An 2013), fungi (Lipovsky et al. 2011), and water organisms such as fish (Vevers and Jha 2008) and *Daphnia magna* (Li et al. 2014). In most of the studies, ecotoxicity was related to the concentration of NPs as well as intensity of irradiation. Increased ecotoxicity of CuO NPs (Dasari et al. 2013), ZnO NPs (Lee and An 2013), and QDs¹ (Derfus et al. 2004) was also determined when nanoparticles were irradiated with UV light. In this section, we discuss how irradiation of photocatalytic NPs can influence their toxicity and what observations have been obtained so far.

8.7.1 Photocatalytic ROS generation

Semiconductor nanoparticles have the characteristic that electrons in the valence band are transferred to the conduction band when appropriate energy is absorbed (see Sect. 8.2). The generating electron–hole pair react with water and oxygen to produce ROS. The negative effects from excess ROS inside the cells are described in Sect. 8.6.1. The ROS concentration and their types are intensively dependent on the bandgap energy of the nanoparticles. As we know, nanoparticles with conduction band (CB) energy less than the redox potential of $O_2/O_2^{\cdot-}$ (−0.2 V) participate to generate superoxide radicals, whereas other nanoparticles that provide valence band (VB) energy equal to or higher than the redox potential of $H_2O/\cdot OH$ (2.2 V) are expected to improve the generation of hydroxyl radicals, which are the most biologically destructive form of ROS (Miller et al. 2012). Generally, the photocatalytic efficiency of a nanoparticle is evaluated by degradation of a substrate by following detection of the product with different chemical or optical properties. In addition, detection of free radicals by electronic paramagnetic resonance (EPR) is a confirmed method for definition of photocatalytic activity of a nanomaterial and has been recommended in some phototoxicity studies. As for photocatalytic efficiency, the ecotoxic effect has a relationship with particle dosage and light intensity.

¹Quantum dots.

Moreover, parameters such as particle size and crystal structure have displayed an influence on phototoxicity. Evidence suggests that the potent TiO₂ P25 NP is more toxic than other TiO₂ NPs form whereas rutile forms show less toxicity than anatase phase particles (Xue et al. 2010). In addition, nanoparticles have a stronger toxic potential for photodegradation than their bulk counterparts, likely because of their greater surface-to-volume ratio, prompting a higher sorption efficiency of light, although detected photocatalytic activity of a nanoparticle does not necessarily supply phototoxicity. For example, in a study by Tong et al. (2013), rutile TiO₂ NPs degraded methylene blue (MB) but did not cause any toxicity to *E. coli*. Evaluation of an ecotoxic hazard towards organisms and cells has been carried out in vivo and in vitro. In case of vitro tests, traditional methods are adapted and an irradiation light source is contained as an additional parameter. To allow a logical conclusion, it is essential to maintain truly identical conditions during both conditions (dark and light) and to make known appropriate negative controls that demonstrate the effect of light or nanoparticles on the cells. Moreover, in common cytotoxicity tests, exactly the production of ROS and their effect on cellular matters are considered, as this is assumed to be the main cause of photo-induced cell death. ROS levels were in fact significantly increased when cells or organisms were similarly exposed to both TiO₂ nanoparticles and light irradiation. The ecotoxic effect has been derived from improved GSH depletion, increased SOD activity, or lipid peroxidation (Dasari et al. 2013). In addition, improved LDH² release is mostly taken as an indicator for ecotoxicity (Rozhkova et al. 2009). The identification and detection of ROS might be applied in both the absence or in the presence of cells. Commonly, the ROS levels can be tested by detection of fluorescent dyes such as H₂DCFDA. As H₂DCFDA does not recognize different radicals but is reduced by some reactive species that present in the cells, the hydroxyl radical sensitive dye (APF) is increasingly applied (Friehs et al. 2016). The generation of hydroxyl radical has been obtained by APF conversion for ZnO and TiO₂ NPs in *Daphnia magna*, *E. coli*, and HeLa cells (Friehs et al. 2016). The production of ROS by photocatalytic NPs such as TiO₂ and several effects observed on cellular members, as well as the mechanisms considered for cellular destruction, are depicted in Fig. 8.7.

Characterization of the radical species has also been applied by some scavenging tests that give some information on the radical formation of irradiated TiO₂ particles in cellular systems. Many scavengers that are applied indicate a selectivity towards a radical species. Evidence from its cellular function shows SOD can be applied as a specific superoxide anion scavenger, whereas catalase converts hydrogen peroxide (Friehs et al. 2016).

Natural materials have been obtained for quenching of •OH radicals: mannitol (Rozhkova et al. 2009), or L-tryptophan (Cai et al. 1992), or H₂O₂ (sodium pyruvate). Scavengers for cell-free systems are DMSO³ (•OH), sodium azide (•O₂ and

²Lactate dehydrogenase.

³Dimethyl sulfoxide.

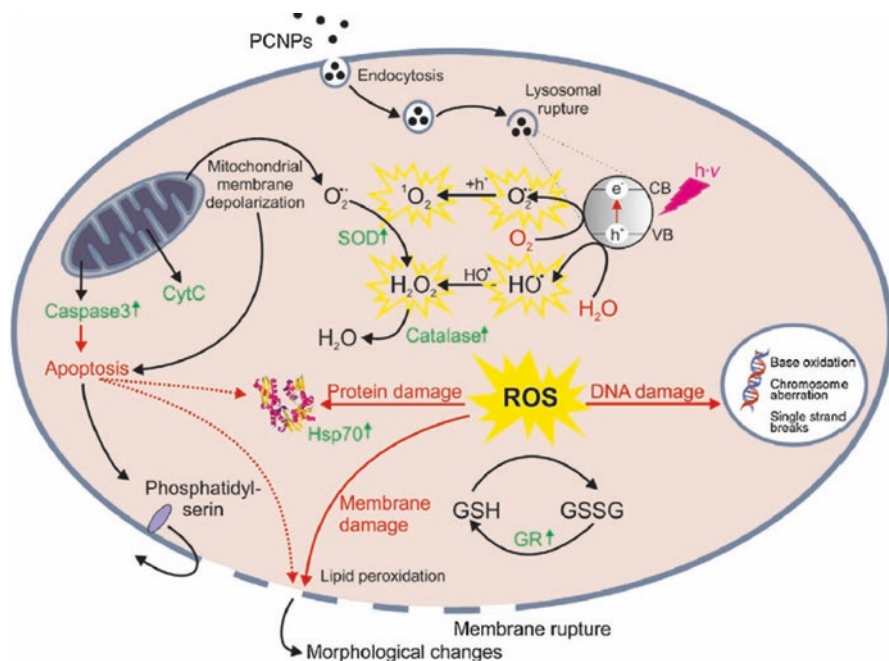


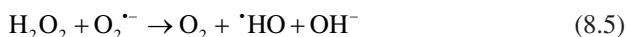
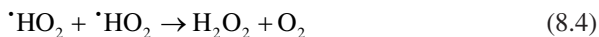
Fig. 8.7 ROS generation by photocatalytic NPs and the effects on cellular members. (From Friehs et al. 2016)

$\cdot\text{OH}$), and dyes such as singlet oxygen sensor green dye. In addition to SOD, Tiron⁴ has been applied to detect superoxide radicals (Idris et al. 2014).

Moreover, Fenoglio and coworkers (2009) explained a mechanism involving the electron transfer (e^-) to an acceptor compound, that is, dissolved oxygen, to generate superoxide anion. The carbon-centered free radicals thus produced can initiate the multistep reactions that cause oxidative destruction of biological molecules such as lipids or nucleic acids (Dalai et al. 2012). Other studies supposed the ROS generation under dark conditions to be carried out by extracellular sorption of nano TiO_2 inducing intracellular ROS production (Dalai et al. 2012). Lakshmi Prasanna and Vijayaraghavan (2015) reported another mechanism for generation of ROS from ZnO nanoparticles in dark conditions. They confirmed the EPR studies of ZnO NP in dark condition in the presence of singly ionized oxygen vacancy that induced the oxygen reaction from the atmosphere with an electron from the ZnO NP surface to generate a superoxide and hydroxyl radicals, respectively (Eqs. 8.2, 8.3, 8.4, and 8.5):



⁴Disodium 4,5-dihydroxy-1,3-benzenedisulfonate.



Moreover, ROS production is supposed to be the main inductor of improved cell death by the irradiated photocatalytic NPs, although induction of oxidative stress does not always relate to photocatalytic activity of a nanoparticle. Some researchers (Dasari et al. 2013) found improved LDH release and GSH depletion in *E. coli* for CuO nanoparticles under irradiation conditions, but no improved ROS generation. Thus, other effects towards photocatalytic degradation of cellular compounds might cause light-induced toxicity. Lipovsky et al. (2011) indicated that smaller ZnO NPs inhibit the growth of the fungus *Candida albicans* more than larger particles. Here, enhancement in toxicity was correlated with a more possible dissolution of Zn^{2+} ions from smaller sizes. In case of unstable particles such as CuO, ZnO, or CdSe, simultaneous irradiation caused increased release of free ions, resulting in higher toxicity. ZnO undergoes dissolution either in acidic conditions or under UV radiation, as shown by the following reaction mechanisms (Han et al. 2010):



The photo-generated holes on ZnO NP surfaces can migrate the ZnO bond and finally oxidize ZnO to Zn^{2+} . Simultaneously, CdSe suffers dissolution reactions, when the photo-generated holes release Cd^{2+} from CdSe (Xi et al. 2011). The released ions can produce ROS by the Fenton reaction or damage cellular pathways (Rahman et al. 2013).

8.8 Conclusion

The environmental use of nanosized particles and their inadvertent release exposes aquatic plants, algae, and fungi to these materials. However, there is considerably less information on several key aspects, which prevents a better evaluation of the ecotoxicity of NPs to these ecosystem organisms. According to the unique physico-chemical characteristics of nanoparticles, hazard assessment is a challenge, and NP–cell interactions are not fully known. Several challenging questions are still unanswered: (a) the related nanoparticle concentrations in aquatic and aerial environments, (b) the physicochemical properties of the NPs and exposure routes, (c) the specific properties that are correlated to the ecotoxicity effects of NPs, and (d) the mechanisms permitting NPs to pass through cell walls and cellular membranes. For particles that are applied in the field of photocatalysis, explanation of the ecotoxic mechanisms for photocatalytic NPs as well as stability of the evaluations are essential factors to investigate the potential ecotoxic effects referring to characterization of materials. This chapter indicated that the consideration of light irradiation

in ecotoxicity tests of photocatalytic NPs has in fact an outcome for endpoint assessment for many organisms that is not negligible. On the other hand, evidence shows that even agglomerated NPs can be more toxic because of their solubility or other specific characterization. Databases based on these ecotoxicity tests may contribute to clarify some of the knowledge concerning photocatalytic NP–cell interactions to increase the quality of ecotoxicity studies.

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