



Impact of natural organic matter on particle behavior and phototoxicity of titanium dioxide nanoparticles



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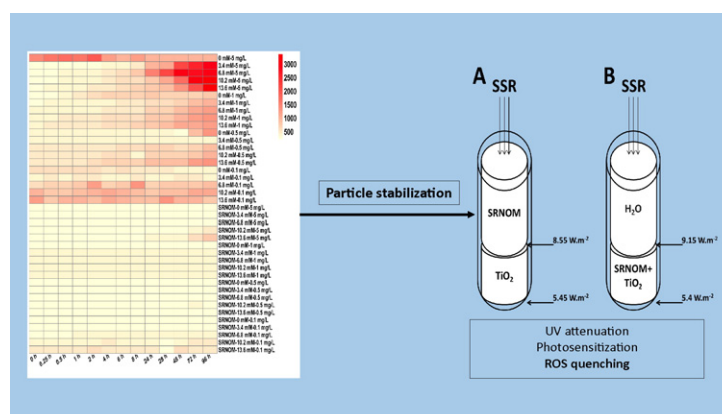
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HIGHLIGHTS

- Impact of natural organic matter (NOM) was studied on nano-TiO₂ phototoxicity.
- Agglomeration size of nano-TiO₂ was stabilized by NOM.
- A global model was developed for prediction of nano-TiO₂ agglomeration size.
- Power analyses suggested the importance of exposure duration and sampling frequency.
- Reactive oxygen species was quenched by NOM.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to their inherent phototoxicity and inevitable environmental release, titanium dioxide nanoparticles (nano-TiO₂) are increasingly studied in the field of aquatic toxicology. One of the particular interests is the interactions between nano-TiO₂ and natural organic matter (NOM). In this study, a series of experiments was conducted to study the impacts of Suwannee River natural organic matter (SRNOM) on phototoxicity and particle behaviors of nano-TiO₂. For *Daphnia magna*, after the addition of 5 mg/L SRNOM, LC50 value decreased significantly from 1.03 (0.89–1.20) mg/L to 0.26 (0.22–0.31) mg/L. For zebrafish larvae, phototoxic LC50 values were 39.9 (95% CI, 25.9–61.2) mg/L and 26.3 (95% CI, 18.3–37.8) mg/L, with or without the presence of 5 mg/L SRNOM, respectively. There was no statistically significant change of these LC50 values. The impact of SRNOM on phototoxicity of nano-TiO₂ was highly dependent on test species, with *D. magna* being the more sensitive species. The impact on particle behavior was both qualitatively and quantitatively examined. A global predictive model for particle behavior was developed with a three-way interaction of SRNOM, TiO₂ concentration, and time and an additive effect of ionic strength. Based on power analyses, 96-h exposure in bioassays was recommended for nanoparticle–NOM interaction studies. The importance of reactive oxygen species (ROS) quenching of SRNOM was also systematically studied using a novel exposure system that isolates the effects of environmental factors. These experiments were conducted with minimal impacts of other important interaction mechanisms (NOM particle stabilization, NOM

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UV attenuation, and NOM photosensitization). This study highlighted both the particle stabilization and ROS quenching effects of NOM on nano-TiO₂ in an aquatic system. There is an urgent need for representative test materials, together with key environmental factors, for future risk assessment and regulations of nanomaterials.

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1. Introduction

Since the discovery of photoelectrochemical water splitting on titanium dioxide (TiO₂) electrodes, a new era began in heterogeneous photocatalysis (Fujishima and Honda, 1972). One of the most active research fields is the development of ever more photoactive TiO₂, such as those manufactured in the nanoscale (nano-TiO₂). Nano-TiO₂ and related nanocomposites have been used in several applications including in paints, cosmetics, solar voltaics, decontamination, and other applications (Leary, 2011; Lizama et al., 2001; Woan et al., 2009). With the continuous growth of the global market for photoactive nanomaterials and their inevitable environmental release, ecological risk assessors are increasingly challenged to assess the risk of photoactive nanomaterials (Li et al., 2013c; Ma et al., 2014; Mueller and Nowack, 2008).

As suggested from decades of research on ambient particles, current nanotoxicological studies indicate that reactive oxygen species (ROS) generation and resultant oxidant injury are the primary mechanisms of toxicity for photoactive nanomaterials such as nano-TiO₂ (USEPA, 2003; Nel et al., 2009; Xia et al., 2009; Tang et al., 2015). The initial process is the generation of ROS. For nano-TiO₂, ROS are generated by the interaction of water or oxygen with an electron–hole pair, generated by light absorption with energy equal to or greater than the void energy region (band gap), a region that extends from the top of the filled valence band to the bottom of the vacant conduction band (Li et al., 2013c; Ma et al., 2012c). Once ROS are generated, various perturbations to biological pathways can occur, such as those in redox systems (glutathione, thioredoxin, etc.), mitochondria-mediated pathways and eventually resulting in apoptotic cell death. Various pathologies can also emerge due to ROS related disruption of intracellular redox homeostasis and irreversible oxidative damage of macromolecules (Halliwell and Cross, 1994; Venditti et al., 2013). Though toxic mechanisms have been extensively addressed in nanotoxicological studies, effective environmental regulations encourage the full range of toxicological investigations, especially those that could contribute to a proper establishment of dose–effect assessment. This effort can be challenged by various confounding factors in the natural environment, of which a particular concern is natural organic matter (NOM).

Some studies have investigated the impacts of NOM on the phototoxicity of nanomaterials. Unfortunately, inconsistent results were reported (Carlos et al., 2012; Grillo et al., 2015; Yang et al., 2013). Most studies reported that NOM reduced toxicity of nanomaterials to the majority of the organisms, although several studies discovered increased toxicity to zebrafish and *Escherichia coli* with the presence of NOM (Gao et al., 2009; Grillo et al., 2015; Yang et al., 2013). The complex interaction mechanisms between NOM and nano-TiO₂ should be taken into consideration in future aquatic toxicological studies of nano-TiO₂. NOM is composed of humic and fulvic materials which are derived from terrestrial soils, vegetation, and microbial activities. Chemically, it is a dynamic mixture of aromatic and aliphatic hydrocarbon structures with different size, structures, and physicochemical properties. NOM is ubiquitous and decades of research has confirmed its importance in redox reactions, chemical fate, element cycling, and microbial activities in aquatic systems (Aeschbacher et al., 2010; Appiani et al., 2014). NOM absorbs UV radiation and short-wavelength visible light, hence it is known to be one of the primary attenuators of underwater UV radiation for freshwater biota (Anesio et al., 2005; Hader et al., 2007; MJ et al., 1996). At the same time, NOM acts both as a photosensitizer and also a ROS quencher. The photosensitizing properties are due to the generation of triplet NOM and ROS by excitation of aromatic ketones,

aldehydes or quinone moieties, and the quenching properties are likely linked to the redox properties of hydroquinone and phenol moieties (Golanoski et al., 2012; Nurmi and Tratnyek, 2002). Studies frequently confirm that NOM plays an important role in agglomeration and/or aggregation size distributions of nanomaterials in natural environments, which could ultimately change the bioavailability and toxicity of nanomaterials (Erhayem and Sohn, 2014; Li et al., 2013a,b; Wang et al., 2009; Yang, 2009). NOM stabilization of nano-TiO₂ is driven by a complex combination of electrostatic forces, van der Waals forces, and steric effects (Philippe and Schaumann, 2014), which is further influenced by multiple factors such as molecular structure, charge, hydrophobicity, molecular weight, pH, ionic strength, valence of ions, temperature and others (Erhayem and Sohn, 2014; Petosa et al., 2010; Pettibone et al., 2008). For example, phenol and carboxyl groups of smaller molecules of NOM increased sorption of nano-TiO₂ by Mg²⁺ and Ca²⁺ through cation bridging and surface charge screening, while sorption is decreased by competition with nitrate, carbonate and phosphate (Chowdhury et al., 2013; Erhayem and Sohn, 2014; Petosa et al., 2010; Yang, 2009; Zhang et al., 2009).

In this study, a series of experiments were conducted to isolate and study the influences of NOM (TiO₂ particle stabilization, UV attenuation, and photosensitization/ROS quenching) on the phototoxicity of TiO₂ to *D. magna* and zebrafish larvae under environmentally relevant solar radiation conditions, and ultimately, to illustrate the relative importance of the above mentioned distinct interactions on the mode of action of photoactive nanomaterials in the presence of NOM in aquatic systems.

2. Materials and methods

2.1. Materials

Nano-TiO₂ (Aeroxide TiO₂ P25) was purchased from Evonik Degussa Corporation (NJ, USA). P25 in this study has been fully characterized by The National Institute of Environmental Health Sciences/National Toxicology Program (Research Triangle Park, NC, USA) with an average primary particle size of 25.1 ± 8.2 nm (transmission electron microscope, mean ± SD, n = 100), a Brunauer–Emmett–Teller (BET) surface area of 51.1 m²/g, and a crystalline structure of 86% anatase and 14% rutile (Li et al., 2014a,b; Ma et al., 2012a). In this study, primary particle size was further confirmed in these experiments using HITACHI Analytical-High Resolution Field Emission Scanning Electron Microscope (FE-SEM) and HITACHI H-8100 Transmission Electron Microscope (TEM) (Fig. 1 A and B). Fully characterized Suwannee River 1R101N natural organic matter (SRNOM) was purchased from the International Humic Substances Society. SRNOM has the following properties: ratio of carboxyl to phenolic functional groups, 2.5; elemental composition ratio of C, H, O, N, S, 52.5/4.2/42.7/1.1/0.7; ratio of aromatic to aliphatic carbon, 0.851. Moderately hard reconstituted water (MHRW) was made according to USEPA standard operating procedures (Agency, 2003). MHRW was diluted with distilled water to generate 0%, 25%, 50%, 75%, and 100% MHRW, with 0, 3.4, 6.8, 10.2, 13.6 mM ionic strength, respectively.

2.2. Particle behavior

Particle behavior of nano-TiO₂ was assessed in a series of assays to evaluate the importance of nano-TiO₂ concentration (0.1, 0.5, 1, and 5 mg/L), SRNOM (0 and 5 mg/L), ionic strength (3.4, 6.8, 10.2, 13.6 mM), and exposure duration (0, 0.25, 0.5, 1, 2, 4, 6, 8, 24, 28, 48,

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