



Influence of dissolved organic matter on photogenerated reactive oxygen species and metal-oxide nanoparticle toxicity



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ABSTRACT

The effect of humic acid (HA) or fulvic acid (FA) on reactive oxygen species (ROS) generation by six metal-oxide nanoparticles (NPs) and their toxicities toward *Escherichia coli* was investigated under UV irradiation. Dissolved organic matter (DOM) decreased $\cdot\text{OH}$ generation by TiO_2 , ZnO , and Fe_2O_3 , with FA inhibiting $\cdot\text{OH}$ generation more than HA. The generated $\cdot\text{OH}$ in NPs/DOM mixtures was higher than the measured concentrations because DOM consumes $\cdot\text{OH}$ faster than its molecular probe. None of NPs/FA mixtures produced $\text{O}_2^{\cdot-}$. The generated $\text{O}_2^{\cdot-}$ concentrations in NPs/HA mixtures (except $\text{Fe}_2\text{O}_3/\text{HA}$) were higher than the sum of $\text{O}_2^{\cdot-}$ concentrations that produced as NPs and HA were presented by themselves. Synergistic $\text{O}_2^{\cdot-}$ generation in NPs/HA mixtures resulted from O_2 reduction by electron transferred from photoionized HA to NPs. DOM increased $^1\text{O}_2$ generation by TiO_2 , CuO , CeO_2 , and SiO_2 , and FA promoted $^1\text{O}_2$ generation more than HA. Enhanced $^1\text{O}_2$ generation resulted from DOM sensitization of NPs. HA did not increase $^1\text{O}_2$ generation by ZnO and Fe_2O_3 primarily because released ions quenched $^1\text{O}_2$ precursor ($^3\text{HA}^*$). Linear correlation was developed between total ROS concentrations generated by NPs/DOM mixtures and bacterial survival rates ($R^2 \geq 0.80$). The results implied the necessity of considering DOM when investigating the photoreactivity of NPs.

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1. Introduction

The application of metal-oxide nanoparticles (NPs) leads to their release into natural waters and causes toxicity toward bacteria (Li et al., 2012; Cho et al., 2004). It has been demonstrated that light exposure (UV lamp, xenon lamp, solar, or conventional fluorescent tubes) could enhance the toxicity of metal-oxide NPs toward *Escherichia coli* (*E. coli*) because of their unique electronic structures and high photoactivity (Cho et al., 2004; Brunet et al., 2009). Concerns over the photoinduced toxicity of NPs to bacteria have stimulated study on their photochemical reactivity in natural waters.

Reactive oxygen species (ROS) generation is the major phototoxicity mechanism of metal-oxide NPs toward *E. coli* (Li et al., 2012; Adams et al., 2006; He et al., 2015). Metal-oxide NPs exposed to light could generate superoxide anion ($\text{O}_2^{\cdot-}$), singlet oxygen ($^1\text{O}_2$), and hydroxyl radical ($\cdot\text{OH}$) (Adams et al., 2006;

Ireland et al., 1993). These three types of ROS may jointly contribute to the toxicity of metal-oxide NPs toward *E. coli* (Adams et al., 2006; Ireland et al., 1993). After released into natural waters, NPs will be exposed to dissolved organic matter (DOM) and light from the sun or artificial lighting (Carlos et al., 2012; Dasari and Hwang, 2013). The high surface-to-volume ratios of metal-oxide NPs and the surfactant properties of DOM facilitate sorption of DOM on the surface of NPs (Carlos et al., 2012; Dasari and Hwang, 2013; Lin et al., 2012). Sorption of DOM can subsequently affect the surface charge, stability, photochemical reactivity, and bioavailability of metal-oxide NPs (Lin et al., 2012; Sousa and Teixeira, 2013). Many previous studies have demonstrated that metal-oxide NPs can generate ROS (Li et al., 2012; Ireland et al., 1993). However, little research has examined the role of DOM in ROS generation type and concentration by metal-oxide NPs and their toxicity.

After light absorbance in the 300–500 nm range, DOM can form excited triplet states ($^3\text{DOM}^*$) and hydrated electrons (e^-) through the photoionization reaction (Lee et al., 2013; Dong and Rosario-Ortiz, 2012). It has been demonstrated that $^3\text{DOM}^*$ could photosensitize carbon-based NPs and enhance $^1\text{O}_2$ photogeneration in

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the C_{60} /DOM mixtures (Li et al., 2015). Metal-oxide NPs could release metal ions (Li et al., 2012; Bondarenko et al., 2012), which complex with DOM or $^3\text{DOM}^*$ through their carboxyl, phenolic, or other groups (Prado et al., 2006; Pandey et al., 2000). It would be of interest to see whether the complexation reaction deactivates $^3\text{DOM}^*$ and impacts $^1\text{O}_2$ generation in NPs/DOM mixtures. It has been demonstrated that the photo-produced electron of DOM could be trapped by semiconductor NPs (Vinodgopal, 1994; Vinodgopal and Kamat, 1992). The question that arises is how the injected electron impacts $\text{O}_2^{\cdot-}$ generation in the NPs/DOM mixtures.

Intense efforts have been devoted to investigate the effect of DOM on the toxicity of metal-oxide NPs toward *E. coli* (Ede et al., 2012; Tong et al., 2013; Rincón and Pulgarin, 2005). It has been demonstrated that the presence of DOM significantly decreased the photoinduced toxicity of TiO_2 and CuO toward *E. coli* (Ede et al., 2012; Rincón and Pulgarin, 2005). Humic acid (HA) and fulvic acid (FA) are main components of DOM in surface waters (Lee et al., 2013; Laurentiis et al., 2013). Their distinct physicochemical properties (e.g., chemical composition, molecular structure, and surface charge) result in their different photochemical reactivity (Li et al., 2015; Aguer et al., 1997). The key question that remains to be answered is how the different photochemical reactivity of HA and FA impact of ROS generation from metal-oxide NPs and *E. coli* toxicity.

We have previously investigated the photogeneration of ROS by six metal-oxide NPs (TiO_2 , CeO_2 , ZnO , CuO , SiO_2 , and Fe_2O_3) and their toxicity toward *E. coli* (Li et al., 2012). *E. coli* are selected as model organism because they are light sensitive and recommended by USEPA as indicators of fecal contamination in waters (Cho et al., 2004; Adams et al., 2006). In this study, the effect of DOM fractions (HA or FA) on the generation types and concentrations of ROS ($^1\text{O}_2$, $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$) by six NPs under UV irradiation (365 nm) was investigated. The ROS generation mechanism in the NPs/DOM mixtures was analyzed by the energy and electron transfer between NPs and DOM. Furthermore, we studied the toxicity of NPs toward *E. coli* in the presence of HA or FA, which was then correlated with ROS generated in the NPs/DOM mixtures. This study should benefit the understanding of toxicity of NPs after their entry into UV treatment process or natural waters.

2. Materials and methods

2.1. Photochemical experiments

Chemicals used in this study are provided in section S1 of Supporting Information. Suwannee River HA and FA were purchased from the International Humic Substances Society (Atlanta, GA, USA). The preparation method of DOM stock solutions and the details of NP properties are provided in section S2 of the Supporting Information. For all photochemical experiments, we measured ROS concentration, assessed toxicity, and measured ion release of NPs/DOM mixtures. One hundred mL of the mixtures was irradiated with a 4-W ultraviolet lamp (UVP, San Gabriel, CA, USA). The UV lamp has an output spectrum ranging from 315 to 400 nm with peak intensity at 365 nm (UV-365). The light intensity in the center of the reaction solution was $1.4 \times 10^{-6} \text{ E L}^{-1} \text{ s}^{-1}$. The reaction temperature was maintained at $(22 \pm 2) \text{ }^\circ\text{C}$ by a constant-temperature water bath.

2.2. ESR detection of $\cdot\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$

Production of $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ in the NPs/DOM mixtures was monitored using 5, 5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as spin-trapping agent. 2, 2, 6, 6-Tetramethyl-4-piperidone (TEMP)

was used as spin-trapping agent for $^1\text{O}_2$ detection. The mixture for $\text{O}_2^{\cdot-}$ detection was prepared by mixing 20 μL DMPO (0.5 M), 3 μL NPs dispersed in DMSO (500 mg/L), 3 μL DOM solution (500 mg/L), and 274 μL DMSO. The mixture for $\cdot\text{OH}$ detection was prepared by mixing 20 μL DMPO (0.5 M), 3 μL NP suspension (500 mg/L), 3 μL DOM solution (500 mg/L), and 274 μL DI water. For $^1\text{O}_2$ detection, the mixture was prepared by mixing 6 μL TEMP (4 M), 3 μL NP suspension (500 mg/L), 3 μL DOM solutions (500 mg/L), and 288 μL DI water. The reaction solutions were placed into the cylindrical quartz cell and irradiated by the same ultraviolet lamp. After 30 min, the quartz cell was quickly measured by electron spin resonance spectrometry (ESR; Bruker ESP-300E, Karlsruhe, Germany). The setting of ESR was as follows: (1) microwave power of 10 mW; (2) modulation amplitude of 2.071 G; (3) sweep width of 100 G; (4) center field of 3480 G; and (5) sweep time of 41.943 s. TEMP was oxidized by $^1\text{O}_2$ to 4-oxo-2, 2, 6, 6-tetramethyl-1-piperidinyloxy radical (TEMPO) when $^1\text{O}_2$ was produced. Accordingly, ESR signals for DMPO- $\text{O}_2^{\cdot-}$, DMPO- $\cdot\text{OH}$, and TEMPO adducts were used to measure $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, and $^1\text{O}_2$ formation, respectively.

2.3. Measurement of $\cdot\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ concentrations

The molecular probe assays were conducted to confirm the photogeneration of ROS and measure their concentrations. One hundred mL of reaction solution containing 5 mg/L NPs and 5 mg/L DOM was placed into a beaker and irradiated by the same UV lamp. The concentration of metal-oxide NPs was set at 5 mg/L because it was difficult to measure the production amount of ROS at lower concentration of NPs by the molecular probe assays. DOM concentration was set at 5 mg/L because it was the lowest concentration allowing a reliable measurement of ROS generation concentrations by DOM with molecular probe method. In addition, 5 mg/L was within the scope of DOM concentrations in natural waters that range from several hundred ng/L to around 10 mg/L (Thurman and Malcolm, 1994). No buffer solutions were added to the reaction solutions to prevent the possibility of colloidal instability during the photochemical experiments. Furfuryl alcohol (FFA, 0.85 mM), *p*-chlorobenzoic acid (pCBA, 20 μM), and XTT (200 μM) were used as molecular probes for $^1\text{O}_2$, $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$, respectively. XTT reduction by $\text{O}_2^{\cdot-}$ results in the formation of XTT-formazan, which has an adsorption peak at 470 nm. Many previous studies have demonstrated that XTT and XTT-formazan were stable under UV-365 irradiation (Brunet et al., 2009; Li et al., 2014; Cai, 2013). After UV illumination, the reaction solutions were sampled, prepared, and analyzed with a high-performance liquid chromatograph (HPLC, Dionex U3000, USA) or UV-vis spectrophotometer (Beckman, DU 7700, Brea, CA, U.S.A.) (Li et al. 2013, 2014; Jin et al., 2013). The time-averaged molar concentration of each ROS was calculated according to published integration function (Li et al., 2012, 2014, 2013).

2.4. Assessment of toxicity

The spread plate method was used to evaluate the effect of DOM on phototoxicity of various NPs. The culture, harvest, plate, and counting methods are provided in section S3. One hundred mL of bacteria suspension (10^5 colony-forming units (CFU)/mL) supplemented with 5 mg/L NPs and 5 mg/L DOM were irradiated by the same UV lamp. After 2 h of irradiation, the suspensions were collected, diluted, and plated onto LB agar plates, which were incubated at $37 \text{ }^\circ\text{C}$ overnight before counting the number of viable bacterial colonies. The survival rates of *E. coli* were presented as the log values of the percentage of surviving bacteria, which was calculated by Eq. (1):

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