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The potential phototoxicity of nano-scale ZnO induced by visible light on freshwater ecosystems

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HIGHLIGHTS

- Visible light led to high solubility of nanoZnO.
- Fungal sporulation capacity was inhibited by L+,Z+.
- Carbon metabolic activity was promoted by L+,Z+.
- No difference of decomposition rate was observed between L+,Z+ and L-,Z+.

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ABSTRACT

With the development of nanotechnology, nanomaterials have been widely applied in anti-bacterial coating, electronic device, and personal care products. NanoZnO is one of the most used materials and its ecotoxicity has been extensively studied. To explore the potential phototoxicity of nanoZnO induced by visible light, we conducted a long-term experiment on litter decomposition of *Typha angustifolia* leaves with assessment of fungal multifaceted natures. After 158 d exposure, the decomposition rate of leaf litter was decreased by nanoZnO but no additional effect by visible light. However, visible light enhanced the inhibitory effect of nanoZnO on fungal sporulation rate due to light-induced dissolution of nanoZnO. On the contrary, enzymes such as β-glucosidase, cellobiohydrolase, and leucine-aminopeptidase were significantly increased by the interaction of nanoZnO and visible light, which led to high efficiency of leaf carbon decomposition. Furthermore, different treatments and exposure time separated fungal community associated with litter decomposition. Therefore, the study provided the evidence of the contribution of visible light to nanoparticle phototoxicity at the ecosystem level.

1. Introduction

Engineered nanoparticles (NPs) have been developed in large quantities for extensive applications (Keller et al., 2013), which will increase their introduction into the environment inevitably (Gottschalk et al., 2013). Based on this, the concerns about NP impacts on human and environment health have been raised and studied in the field of nanotoxicology and ecotoxicology (Jain, 2017; Oberdörster et al., 2005). Among these NPs, zinc oxide (ZnO) is widely used due to its unique properties of UV-absorbance efficiency, small particle size, high mechanical strength, and surface area to volume ratio (Ma et al., 2013; Yin et al., 2015), which can potentially contribute to its toxicity (Ma et al., 2013).

Current studies have showed that ZnO NPs can be harmful to a large spectrum of aquatic organisms, such as microalgae (Cai et al., 2016), *Daphnia* (Bacchetta et al., 2017), *Ceriodaphnia* (Bhuvaneshwari et al., 2016), earthworms (Li et al., 2011a), and fishes (Zhao et al., 2016). The toxicities of ZnO NP may be attributed to its photocatalytic activity, because ZnO NP can promote generation of reactive oxygen species under light irradiation, induce oxidative stress, and eventually elicit toxicity (Applerot et al., 2009;

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Lee and An, 2013; Ma et al., 2011; Yin and Casey, 2015; Zhang et al., 2008). The photoactive materials have efficient ability for the absorption of light in the UV (290–400 nm), visible (400–750 nm) or near infrared (750–950 nm) range (Choi, 2016; Larson and Berenbaum, 1988). The visible light is one of the most important parts of light source, but studies on the phototoxicity induced by visible light are scarce. There is difference of phototoxicities on *Caenorhabditis elegans* induced between artificial light and natural light (Ma et al., 2011), which highlights the importance of exploring the potential phototoxicity of ZnO NP induced by visible light to the natural biota.

Leaf litter decomposition is regarded as a bioassessment tool of nanomaterial effects on the aquatic ecosystems, because it is a key ecosystem-level process driven by the decomposers in streams (Bärlocher and Boddy, 2016; Bour et al., 2016; Batista et al., 2017; Pradhan et al., 2011; Tlili et al., 2017). Aquatic fungi, as the main microbial decomposers, can release extracellular enzymes to degrade the structural polysaccharides of leaf cell wall and improve palatability to invertebrate shredders (Naiman and Bilby, 1998). They are observed in the streams polluted by Zn ion (Azevedo et al., 2007; Medeiros et al., 2010) or the mixtures of Zn ion and phosphate (Fernandes et al., 2009). These findings increase the interest in better understanding of the fungal contributions to leaf litter decomposition under Zn pollution.

The estimated concentrations of ZnO NP were 0.01 and 0.43 $\mu g\,L^{-1}$ in the surface water and the treated wastewater, respectively (Gottschalk et al., 2009). Based on Gottschalk et al.'s estimates, many studies on the freshwater ecosystems chose NP concentrations in low levels (Gottschalk et al., 2013). For example, Tlili et al. designed a leaf decomposition experiment involved three levels of AgNP addition (0, 0.05, and 0.5 μM) (Tlili et al., 2017). Colman et al. conducted a wetland mesocosm experiment involved two sizes of AgNP addition (12 and 49 nm) at a concentration of 2.5 mg Ag L^{-1} (Colman et al., 2014). However, few studies focus on NP effects with high concentrations (Pradhan et al., 2011, 2015), given that the environmental level is expected to increase continually due to the widespread application of these nanomaterials. Therefore, it is necessary to investigate the harmful effects of ZnO NP at higher concentrations related to certain pollution incidents in freshwater ecosystems (e.g. spill scenarios).

Furthermore, risk assessment of NPs requires understanding the potential effects of environmental conditions on the fate of NPs, such as chemical stressor, organic matter, UV radiation (Gessner and Tlili, 2016). For example, Pradhan et al. assessed the combined effects of humic acid and various sizes of CuO NP on the microbial decomposers and leaf decomposition in stream ecosystems (Pradhan et al., 2016). Therefore, the present study aimed to evaluate the potential phototoxicity of ZnO NP induced by visible light. The specific questions about the combined effects of ZnO NP (100 mg L^{-1}) and visible light were as follows: (1) does visible light affect solubility of ZnO NPs in stream water; (2) what are the consequence of the combined effects on fungal conidial productions, metabolic activities, and community structures; (3) do any effects on fungal functions have consequences for litter decomposition? To answer these questions, a microcosm experiment was conducted on *Typha angustifolia* leaf decomposition during long-term exposure (158 days).

2. Materials and methods

2.1. Suspension of ZnO NPs

ZnO NPs with an advertised particle size of 30 ± 10 nm (99.9% metals basis) were provided as powders by Aladdin Industrial Inc. (Shanghai, China). The stock suspension (6 g L^{-1}) was developed by dispersing the ZnO NPs in deionized water using a digital ultrasonic cleaner (KQ-500DE, Kunshan, China) at 40 kHz for 30 min. The morphology of ZnO NP in the stock suspension was characterized using transmission electron microscopy (JEM-2010, JEOL, Japan) (Fig. S1, average size 15 ± 3 nm). The optical property of the ZnO NPs in stream water was measured by recording their UV–vis spectra in the 200–800 nm range (TU-1810PC, PERSEE General Instrument Inc., Beijing, China) (Fig. S2).

2.2. Preparation of Typha angustifolia leaf litter

Typha angustifolia leaves were collected from the Yellow River Basin (Jiyuan, China), which were extensively washed, cut into fragments (2 cm), and oven dried at 40 °C to a constant weight. Sets of the leaf fragments (n = 60) were subsequently enclosed in the fine mesh bags (15 × 15 cm, 0.5 mm mesh size). In spring 2016, a total of sixty-six litter bags were immersed in a stream belonging to the Yellow River (34°56′24.73″N, 112°25′56.15″E, 134.5 m altitude) for microbial colonization. After 2 weeks, all the litter bags were retrieved, placed into a cool box with stream water, and then returned to the laboratory. During the period of microbial colonization, the physicochemical parameters of stream water were monitored every 2 d in situ by a HQ Series Portable Meter (ProPlus, YSI, USA) and showed in Table S1. Stream water (30 L) was collected and stored at −20 °C until use.

2.3. Microcosm experiment

The leaf fragments from each litter bag were gently rinsed with deionized water and placed into 150 mL sterile Erlenmeyer flasks (n = 63) with 80 mL of the filtered (Whatman®, 1.2 μm pore size) and sterilized (121 °C, 30 min) stream water. The microcosm experiment involved four treatments: (1) L-,Z-: leaves were incubated in the dark without ZnO NPs, (2) L+,Z-: leaves were incubated in the light without ZnO NPs, (3) L-,Z+: leaves were incubated in the dark with ZnO NPs (100 mg L^{-1}), and (4) L+,Z+: leaves were incubated in the light with ZnO NPs (100 mg L^{-1}). All treatments were replicated 3 times. The visible light was supplemented by fluorescent lamps with an intensity of 28 $W\,m^{-2}$ (400–750 nm). The dark treatment was achieved by wrapping the microcosms in black cloth. All microcosms were shaken at 150 r min^{-1} under 18 °C. The stream water was renewed each week including ZnO NPs. Leaf fragments were sampled immediately and after 16, 36, 61, 110, and 158 d to determine the leaf mass loss, dehydrogenase activity, extracellular enzyme activities, and the sporulation rate and diversity of the associated aquatic hyphomycetes.

2.3.1. Leaf mass loss

Leaf fragments from each microcosm were gently rinsed with deionized water to remove the attached white particles (ZnO NPs) and dried at 40 °C for 72 ± 24 h to obtain a constant mass. Then they were weighed to the nearest 0.001 g to determine the leaf mass loss (Du et al., 2017a), which was expressed as the mass remaining subtracted from the initial leaf dry mass. Decomposition rate was calculated by the exponential equation: (Olson, 1963): $X_t = X_0 e^{-kt}$, where X_0 is the initial mass, and X_t is the remaining mass at time t, k is the decomposition rate ($month^{-1}$).

2.3.2. Leaf carbon and nitrogen contents

Nutrient analysis was done to determine the total carbon (C) and nitrogen (N) contents of the leaves after 158 d exposure. Briefly, the leaf fragments were dried at 90 °C and ground to a fine consistency. Total C and N contents were measured using an automatic elemental analyzer (VARIO EL III, Elemental Analysensysteme