Nano-TiO₂ both increases and decreases arsenic toxicity: Evidence from different aquatic animal experiments

Z.X. Luo^{1,2}, Z.H. Wang², F. Yang¹ & C.Z. Yan¹

¹Key Laboratory of Urban Environment and Health, Institute of Urban Environment,
Chinese Academy of Sciences, Xiamen, P.R. China

²College of Chemistry and Environment, Fujian Province Key Laboratory of Modern Analytical Science and
Separation Technology, Minnan Normal University, Zhangzhou, P.R. China

ABSTRACT: Titanium dioxide nanoparticles (nano-TiO₂) are usually applied to treat arsenic-polluted drinking water. Additionally, wide application of nano-TiO₂ can enter into the environment inevitably. Furthermore, titanium dioxide nanoparticles (nano-TiO₂) can adsorb ambient pollutants to modify their bioavailability in aquatic organisms, as well as their toxicity of its ambient pollutants. This study investigated arsenic accumulation, subcellular distribution and toxicity on two aquatic animals (*Daphnia magna* in freshwater and *Artemia salina* in salt water). Nano-TiO₂ acts as a positive carrier, significantly facilitating *D. magna*'s ability to uptake As(V) as well as *Artemia salina*. In *Artemia salina*, As percentage in biologically active metal (BAM) fractions significantly decreased after the addition of 10 mg L⁻¹ of nano-TiO₂, while the fractional percentage of As increased in cellular debris. These lower As proportions in the sensitive fractions of cells indicate As(V) toxicity inhibition. Higher As(V) EC₅₀ values in nauplii (by a magnitude from 1.97 to 2.76) compared to the control (nano-TiO₂ free) as we increased nano-TiO₂ concentrations from 1 to 1000 mg L⁻¹, indicates that nano-TiO₂ could alleviate As(V) toxicity in *A. salina* nauplii by enhancing efflux and decreasing the proportion of As in the sensitive fractions of cells. In contrast, in *D. magna*, even though As accumulation increased with increasing nano-TiO₂ concentrations in *D. magna*, As(V) toxicity associated with nano-TiO₂ exhibited a dual effect. Compared to the control, the increased As was mainly distributed in BDM (biologically detoxified metal), but Ti was mainly distributed in MSF (metal-sensitive fractions) with increasing nano-TiO₂ levels. Differences in subcellular distribution demonstrated that adsorbed As(V) on nano-TiO₂ could dissociate itself and be transported separately, which results in increased toxicity at higher nano-TiO₂ concentrations. Decreased As(V) toxicity associated with lower nano-TiO₂ concentrations results from unaffected As levels in MSFs (when compared to the control), where several As components continued to be adsorbed on nano-TiO₂. Accordingly, arsenic toxicity on aquatic animals by nano-TiO₂ depends on animal species and the behaviors of the co-contaminants inside, especially their assimilation in the digestive tract. More attention should be paid to the influence of nano-TiO₂ on As(V) assimilation in the digestive tract.

1 INTRODUCTION

Arsenic (As) is a metalloid included in the priority list of hazardous substances. This is a result of its high toxicity and wide distribution. Potential health hazards and environmental impacts of manufactured nanoparticles (MNPs) have become a significant concern with the rapid development of nanotechnology. It has been well established that nano-TiO₂ has the potential to facilitate the entry of co-contaminants adsorbed by nanoparticles into aquatic organisms and to subsequently promote potential toxic effects (Li *et al.*, 2016; Yan *et al.*, 2017). However, little available information describes the impact of nanoparticles on biokinetics

of various co-contaminants in aquatic organisms, particularly for the spatial and subcellular distribution of co-contaminants associated with nanoparticles.

Titanium dioxide nanoparticles (nano-TiO₂) are usually applied to treat polluted drinking water by arsenic (Yan *et al.*, 2017). Additionally, wide application of nano-TiO₂ can enter into the environment inevitably. Most previous relevant studies observed that As(V) is strongly adsorbed to TiO₂ nanoparticles and could subsequently affect chemical accumulation. Arsenic toxicity on aquatic animals by nano-TiO₂ depends on animal species and the behaviors of the co-contaminants inside, especially their assimilation in the digestive tract. This study investigated arsenic

Figure 1. Subcellular distribution in *D. magna*.

accumulation, subcellular distribution and toxicity on two aquatic animals (*Daphnia magna* in freshwater and *Artemia salina* in salt water).

2 METHODS

2.1 Subcellular distribution

We determined subcellular partitioning of total As and Ti in two aquatic animals body tissues using the methods of differential centrifugation (Wang *et al.*, 2017). We obtained a total of five different fractions, including cellular debris (containing cell membranes), organelles (containing nuclear, mitochondrial, microsomes, and lysosomes), heat-denatured protein (HDP, containing enzymes), heat-stable protein (HSP, or metallothionein-like proteins), and metal-rich granules (MRG). Results are expressed in mg (dry weight) per individual.

3 RESULTS AND DISCUSSION

3.1 Subcellular distribution of arsenic and titanium

The dissociation of arsenic from nano-TiO₂ of 20 mg L⁻¹ was observed due to the differences of

Figure 2. Subcellular distribution in *A. salina*.

subcellular distribution of arsenic and titanium in *D. magna*, resulting in the higher toxicity of arsenate in higher levels of nano-TiO₂ (Fig. 1).

However, decreased As(V) toxicity associated with lower nano-TiO₂ concentrations results from unaffected As levels in MSFs (when compared to the control), where several As components continued to be adsorbed by nano-TiO₂ (Fig. 1).

Arsenic percentage in biologically active metal (BAM) fractions significantly decreased, decreasing As(V) toxicity on *A. salina* (Fig. 2).

ACKNOWLEDGMENTS

This study was jointly supported by the National Nature Science Foundation of China (project nos. 41401552, 41271484 and 21277136) and the Nature Science Foundation of Fujian Province (2016J01691).

REFERENCES

- Li, M., Luo, Z., Yan, Y., Wang, Z., Chi, Q., Yan, C. & Xing, B.S. 2016. Arsenate accumulation, distribution, and toxicity associated with titanium dioxide nanoparticles in *Daphnia magna*. *Environ. Sci. Technol.* 50(17): 9636–9643.
- Wang, Z. H., Luo, Z. X., Yan, C. Z. & Xing, B. S. 2017. Impacts of environmental factors on arsenate biotransformation and release in *Microcystis aeruginosa* using the Taguchi experimental design approach. *Water Res.* 118: 167–176.
- Yan, C. Z., Yang, F., Wang, Z. S., Wang, Q. Q., Seitz, F. & Luo, Z. X. 2017. Changes in arsenate bioaccumulation, subcellular distribution, depuration, and toxicity in *Artemia salina nauplii* in the presence of titanium dioxide nanoparticles. *Environ. Sci. Nano.* 4(6): 1365–1376.