Interactions between Plants and Rare Earth Oxide Nanoparticles

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Abstract

Rare earth oxide nanoparticles (REO NPs) can be released into the environment from various application routes, but their effects on the ecosystem are still little known. In this study, we exposed cucumber seedlings to suspensions of La_2O_3 and CeO_2 NPs for 14 d. Phytotoxicity of the two REO NPs was assessed and their distribution and transformation in plant tissues were investigated. CeO_2 NPs had no toxicity to cucumber at all tested concentrations, while La_2O_3 NPs showed significant inhibition on root elongation, biomass, as well as induced more ROS and cell death in roots. The different distribution and speciation of Ce and in plants were determined by synchrotron-based micro X-ray fluorescence microscopy (SR-μXRF) and X-ray absorption spectroscopy (XAS). In the aerial parts, all of La was combined with phosphate or carboxylic group while only a fraction of Ce was changed to Ce(III)-carboxyl complexes, implying that La_2O_3 acted as its ionic form while CeO_2 displayed the behavior of particles or particle-ion mixtures. The higher dissolution of La_2O_3 than CeO_2 NPs might be the reason for their significant difference in phytotoxicity and transporting behaviors in cucumber plants.

Keywords: Biotransformation, Phytotoxicity, Rare earth oxide nanoparticles

1. Introduction

Rare earth oxide NPs is one class of the most important nanomaterials, which are widely used in paint coating, polishing powder, catalysts, luminescent materials, etc. (Kaneko et al. 2007). As a result, the deliberate and accidental release of REO NPs into the environment is inevitable and concerns over the potential impacts that their release may have on human health and the environment are increasing (Khodakovskaya et al. 2011). Plants represent the largest interface between the environment and the biosphere. As part of the first trophic level in the food chain, plants may serve as the primary target and a potential pathway for the transporting of REO NPs. So, it is necessary to determine the response and possible role of plants in the fate and transport of REO NPs.

We previously found suspensions of trivalent REO NPs (La_2O_3, Gd_2O_3 and Yb_2O_3) at 2000 $mg \cdot L^{-1}$ severely inhibited the root elongation of radish, rape, tomato, wheat, cabbage, and cucumber. On the contrary, CeO_2 NPs had no negative effect on the 6 plant species. In this study, we made an attempt to clarify relations between the chemical reactivity (dissolution) of CeO_2 and La_2O_3 NPs and their behaviors in cucumber plants. This research provides substantial evidence that chemical reactivity is an important factor to investigate the toxicity of metal- and metal oxide-based NPs.

2. Methods

2.1. Nanoparticles

La_2O_3 NPs were purchased from Sigma-Aldrich and used as received. CeO_2 NPs were synthesized using a precipitation method as reported previously (Zhang et al. 2011). Physicochemical properties of the two NPs are listed in Table 1.

Table 1. Properties of CeO_2 and La_2O_3 NPs

	CeO_2 NPs	La_2O_3 NPs
Size (nm)	25.2±2.3	23.1±3.8
Crystal form	Fluorite	Cubic
Purity	99.99%	99.9%
DLS[a] (nm)	122.6±20.9	247.3±42.5
DLS[b] (nm)	1125±206	785±159
ζ potential (mV)[a]	34.3±5.1	30.4±3.8
ζ potential (mV)[b]	-10.2±3.5	-8.7±2.7
pH value[b]	6.0±0.2	7.2±0.3

a: in ultrapure water; b: in nutrient solution

2.2. Phytotoxicity experiments

Cucumber (*Cucumis sativus*) was chosen for the phytotoxicity study and treated with CeO_2 or La_2O_3 NPs at different concentrations (0.2, 2, 20, 200, 2000 $mg \cdot L^{-1}$) in 1/4 strength Hoagland solution without phosphate. Root and shoot elongation were measured at the first 5 days and biomass of seedlings was assessed after treatment for 14 d. Oxidative stresses were evaluated by measuring H_2O_2 accumulation and cell death in the roots.

2.3. Synchrotron radiation analysis

Distribution of Ce/La in the cucumber roots and leaves were assessed using SR-μXRF at Shanghai Synchrotron Radiation Facility. XAS spectra of Ce in the samples were collected at Beijing Synchrotron Radiation Facility.

2.4. Data analysis

The results were expressed as mean±SD (standard deviation). One-Way ANOVA followed by Tukey's HSD test was employed to examine the statistical differences.

3. Results and Discussion

The two kinds of representative REO NPs, CeO_2 and La_2O_3 NPs, with similar sizes but different chemical compositions, showed significantly different phytotoxicity and behavior (uptake, translocation, distribution, and biotransformation) in cucumber plants in this research.

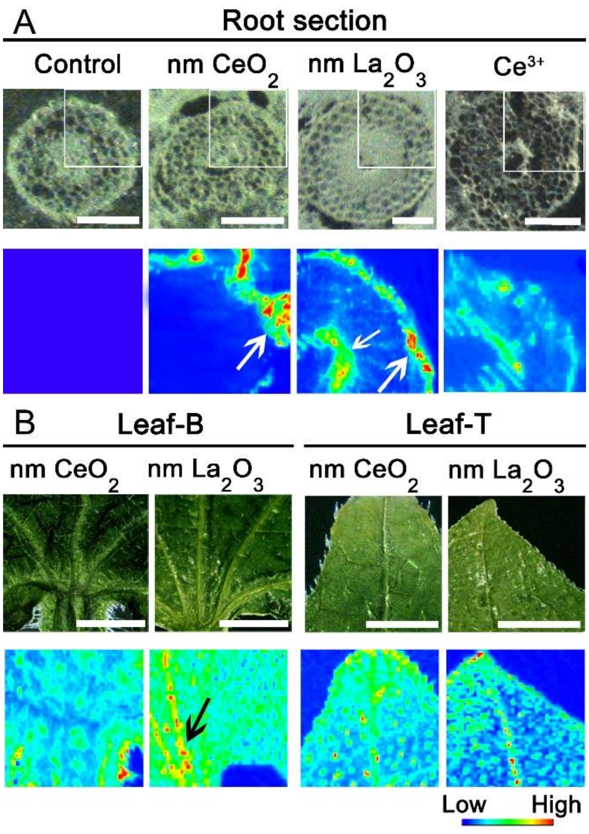

Figure 1. SR-μXRF images of Ce or La in cucumber root sections (A) and leaves (B). Leaf-B means leaf base and Leaf-T means leaf tip).

Phytotoxicity tests indicate that La_2O_3 NPs exposure induced inhibitive effects on seedling elongation and biomass, increase of H_2O_2 content and cell death in comparison with the controls, while CeO_2 NPs at all the applied concentrations had no toxic effect on the cucumber plants. La_2O_3 NPs at 2000 mg/L reduced biomasses of the root and shoot by 65.8% and 42.8% respectively with respect to each control. In the roots that treated with La_2O_3 NPs, a remarkable accumulation of La was found in the peripheral regions of endodermis, around the pericycle, which resemble the trivalent rare earth cations (Figure 1A). In the shoots, all of La was presented as lanthanum carboxylates and $LaPO_4$, which also resemble the trivalent rare earth cations. As for CeO_2 NPs, only little Ce was only found in the cortex and no Ce was detectable in vascular cylinder of the root sections indicating different interactions of Ce species compared to that of La species with root tissues. It is probable that nanoparticle properties dominated the behavior of Ce species in the roots.

The difference in chemical reactivity leads to different dissolution of the two kinds of REO NPs. In nutrient solutions, the amount of La^{3+} ions released from La_2O_3 NPs was much higher than that of Ce^{3+} ions from CeO_2 NPs at each treatment concentration. This was further confirmed by the speciation analysis of Ce and La in plant tissues by XAS. In the roots, only a small amount of CeO_2 NPs (<10%) were dissociated, while a large number of La_2O_3 NPs (>80%) were transformed into lanthanum carboxylates and phosphate. Considering the similar bioeffects of La^{3+} and Ce^{3+} and different dissolution degree of the two NPs in nutrient solutions and plants, it is reasonable to speculate that the higher dissolution degree of La_2O_3 than CeO_2 NPs might be the reason for their significant difference in phytotoxicity.

As a summary, we show that how the physicochemical properties of NPs affect their toxicological effects and distribution and chemical species in plants. The higher degree of dissolution of La_2O_3 than CeO_2 NPs could be responsible for their significant difference in phytotoxicity and transporting behaviors in cucumber plants.

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