



## Chemical transformation of zinc oxide nanoparticles as a result of interaction with hydroxyapatite



Jitao Lv<sup>a</sup>, Shuzhen Zhang<sup>a,\*</sup>, Songshan Wang<sup>a</sup>, Lei Luo<sup>a</sup>, Hongling Huang<sup>a</sup>, Jing Zhang<sup>b</sup>

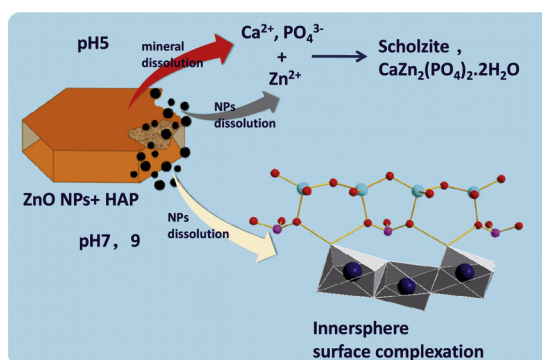
<sup>a</sup> State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

<sup>b</sup> State Key Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

### HIGHLIGHTS

- ZnO NPs undergo chemical transformation in the presence of insoluble phosphate.
- HAP induced the transformation of ZnO NPs to scholzite under acid condition.
- ZnO NPs transformed to amorphous phase under neutral and basic conditions.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 29 April 2014

Received in revised form 10 July 2014

Accepted 22 July 2014

Available online 1 August 2014

#### Keywords:

ZnO nanoparticle  
Chemical transformation  
Hydroxyapatite  
XAFS

### ABSTRACT

Recent studies have revealed that zinc phosphate is an important transformation product of zinc oxide nanoparticles (ZnO NPs) in the environment, and the role of soluble phosphate in the transformation of ZnO NPs to zinc phosphate has been confirmed. However, whether insoluble phosphate that exists widely in the environment can induce chemical transformation of ZnO NPs has not been addressed. Therefore, transformation of ZnO NPs in the presence of hydroxyapatite (HAP), selected as representative of insoluble phosphate, at different pH was investigated in the present study. Transformation products were identified by employing X-ray diffraction and synchrotron based X-ray absorption fine structure spectroscopy. The results indicate that under acidic condition (pH 5) phosphate ion ( $\text{PO}_4^{3-}$ ) and calcium anion ( $\text{Ca}^{2+}$ ) were released from HAP in aqueous solution, inducing a rapid transformation of about 80% ZnO NPs to scholzite within 4 h. Under neutral or basic conditions (pH 7 and 9) the adsorption of  $\text{Zn}^{2+}$  on HAP resulted in a slow transformation of about 60% ZnO NPs to amorphous inner-sphere Zn adsorption complexes within 30 days. This work suggests the important role of HAP in the transformation of ZnO NPs and may affect the behavior, fate and toxic effects of ZnO NPs in the environment.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Over recent decades, engineered nanoparticles (ENPs) are increasingly produced as the result of the rapid development in nanotechnology. The use of ENPs in industrial and household applications will lead to their release into the environment, causing

\* Corresponding author at: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China.  
Tel.: +86 10 62849683; fax: +86 10 62923563.

E-mail address: [sszhang@rcees.ac.cn](mailto:sszhang@rcees.ac.cn) (S. Zhang).

potential ecological and human health impacts [1,2]. Once released into the environment, the large surface area and high reactivity of ENPs cause them to undergo physical, chemical and biological transformations which can affect their environmental behavior and fate [3,4]. For this reason a comprehensive understanding of transformation behaviors of ENPs in the environment is critically important to ensure the safe use of nanomaterials.

Zinc oxide nanoparticles (ZnO NPs) are a common type of engineered nanomaterials that have been widely used in many applications such as catalysts, semiconductors, sunscreen, textiles, paintings, industrial coatings and optics [5]. Model results have suggested that the environmental concentration of ZnO NPs is second only to TiO<sub>2</sub> NPs [6], therefore much concern has been raised about environmental behaviors and implications of ZnO NPs.

Previous researches on behaviors of ZnO NPs have mainly focused on their physical transformations (e.g. aggregation, sedimentation) and dissolution of ZnO NPs in the environment, and the influences of environmental factors such as pH, DOM, ionic strength and co-existence of anions (e.g. SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) on physical transformations of ZnO NPs have been addressed [7–11]. Recently, much attention has been paid to chemical transformations of ENPs in the environment, which will result in largely unknown end products and affect the fate and potential toxicity of ENPs in the environment [4]. For example, studies have demonstrated the transformation of ZnO NPs to ZnS in the presence of sodium sulfide (Na<sub>2</sub>S) or hydrogen sulfide (H<sub>2</sub>S) [12,13]. Our previous research [14] has confirmed that phosphate ions can induce the transformation of ZnO NPs to tetrahydrate Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in aqueous solutions at room temperature and under neutral pH conditions. Very recently, Rathnayake et al. [15] also observed that phosphate ions induced transformation of ZnO NPs to Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and further indicated that such transformation was pH dependent and crystalline hopeite preferred to form at pH 6 rather than at pH 8. These studies were performed under simple laboratory conditions. In actually, wastewater is a major route of introduction of ZnO NPs to the environment. Recently, two field studies have been conducted to investigate chemical transformations of ZnO NPs in wastewater treatment systems. Three transformed species of ZnO NPs including Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, ZnS and Zn associated Fe oxy/hydroxides (Zn-FeOOH) were identified in sludge and biosolids generated by wastewater treatment [16,17]. Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was observed persistent in sludge and biosolids, while the ratio of ZnS and Zn-FeOOH depended on the redox state and water content of the biosolids [17]. Therefore, both laboratory and field researches have demonstrated the importance of the chemical transformation of ZnO NPs to Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and validated the role of phosphate in the transformation of ZnO NPs in the environment. However, due to the strong complex capability of phosphate to minerals and cations such as Ca<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> and heavy metals [18], phosphate very likely exists as insoluble form in natural water and wastewater. It is therefore necessary to elucidate the role of insoluble phosphates in chemical transformation of ZnO NPs in order to understand the phosphatization of ZnO NPs in the environment.

Hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, (HAP)] is an important kind of insoluble phosphate containing minerals [19]. Due to its strong capacity to immobilize metals and radionuclides, HAP and materials containing HAP have been widely used in water treatment [20,21] to efficiently remove metal ions from wastewater through ion exchange at surface sites and coprecipitation [19,22]. Therefore, HAP was selected as a representative of insoluble phosphate containing minerals in the present study to investigate whether and how the presence of insoluble phosphate influence chemical transformations of ZnO NPs. X-ray diffraction (XRD), synchrotron based X-ray absorption fine structure spectroscopy (XAFS) and transmission electron microscopy (TEM) were employed to characterize the transformation products of ZnO NPs in the presence of HAP. The

results of this study are expected to help us better understand the behavior and fate of ZnO NPs in the natural environment.

## 2. Materials and methods

### 2.1. Characterization of materials

ZnO nanoparticles were purchased from Nachen Sci & Tech Co. (Beijing, China) with a purity of 99.9%, the same as described previously [14]. The HAP used was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). The microtopography of HAP, ZnO NPs and the samples were obtained with H-7500 (Hitachi, Japan) transmission electron microscope (TEM) operated at 80 kV. The  $\zeta$  potentials of ZnO NPs and HAP were measured at varied pH in 10 mmol L<sup>-1</sup> NaNO<sub>3</sub> solution with a Malvern Nano ZS (Malvern Instruments, UK).

### 2.2. Batch experiments of reaction between ZnO NPs and HAP

Suspensions of HAP at concentration of 1.0 g L<sup>-1</sup> in 10 mmol L<sup>-1</sup> NaNO<sub>3</sub> solution were adjusted to pH 5.0 ± 0.1, 7.0 ± 0.1 and 9.0 ± 0.1, respectively, and allowed to equilibrate for 24 h. Then ZnO NPs or Zn<sup>2+</sup> were added to reach a concentration of 65.4 mg Zn L<sup>-1</sup>. The ZnO NPs/HAP binary suspensions were placed in conical flasks and shaken at 100 rpm without further pH adjustment. At designated time intervals 10 mL suspensions were extracted over the course of 30 days and then separated by centrifugation at 10,000 × g for 40 min. The residue was washed three times with deionized water and then lyophilized for 24 h in a freeze-dryer (Free Zone 2.5) at -40 °C and under 0.130 mbar pressures. The supernatant was filtered through suction filtration with 0.22 μm microporous membrane (Millipore), Filtrates were acidified with 100 μL HNO<sub>3</sub>, and concentrations of Zn, P and Ca were quantified by ICP-OES (Agilent, 7500c). All batch experiments were carried out in duplicate.

### 2.3. X-ray spectroscopy analysis

The lyophilized powder samples were ground and coated homogeneously on Kapton tape for XAS analysis. Zinc K-edge (9659 eV) X-ray absorption spectra were collected at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF, China) and beamline 14W at the Shanghai Synchrotron Radiation Facility (SSRF, China). A spectral range of -200 to 800 eV from the K-absorption edge of Zn was collected under ambient conditions. Si(111) monochromator crystals were utilized, and Zn foil was used for energy correction. ZnO NPs, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, ZnSO<sub>4</sub> aqueous solution and Zn<sup>2+</sup> adsorbed on HAP (Zn<sub>ads</sub>-HAP) were used as reference compounds. Spectra were collected in transmission mode for the ZnO NPs and Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O powders, and in fluorescence mode for ZnSO<sub>4</sub> aqueous solution, Zn<sub>ads</sub>-HAP and the samples. Standard XAFS data reduction procedures were undertaken using the program package IFEFFIT [23], and WinXAS v 3.1 [24] was used for data fitting. Detailed processes were described previously [14,25]. Simply, background removal, normalization, cubic spline conversion and forward Fourier transform of the  $k^3 \chi(k)$  spectra from 2.4 to 12.5 Å<sup>-1</sup> using Bessel window were performed to obtain the radial distribution function (RDF) in R-space. Theoretical EXAFS amplitudes and phase functions of reference models ZnO, hopeite (Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O) and scholzite (CaZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O) for Zn-O, Zn-Zn and Zn-P associations generated by FEFF 8.2 were fitted to the experimental spectra. An amplitude reduction factor S<sup>0</sup> = 0.87 was determined by the fitting of ZnO with fixed coordination numbers (CN). Analysis of EXAFS oscillations based on this fitting procedure typically provides accuracies for the CN of ±10% and R of ±0.01 Å. X-ray diffraction (XRD) analysis of the samples

Download English Version:

<https://daneshyari.com/en/article/592594>

Download Persian Version:

<https://daneshyari.com/article/592594>

[Daneshyari.com](https://daneshyari.com)