Dissolution and Microstructural Transformation of ZnO Nanoparticles under the Influence of Phosphate

Jitao Lv,[†] Shuzhen Zhang,^{*,†} Lei Luo,[†] Wei Han,[†] Jing Zhang,[‡] Ke Yang,[§] and Peter Christie^{||}

[†]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[‡]State Key Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

[§]Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, China

^{||}Agri-Environment Branch, Agri-Food and Biosciences Institute, Newforge Lane, Belfast BT9 5PX, United Kingdom

S Supporting Information

ABSTRACT: The toxicity and fate of nanoparticles (NPs) have been reported to be highly dependent on the chemistry of the medium, and the effects of phosphate have tended to be ignored despite the wide existence of phosphate contamination in aqueous environments. In the present study the influence of phosphate on the dissolution and microstructural transformation of ZnO NPs was investigated. Phosphate at a low concentration rapidly and substantially reduced the release of Zn^{2+} into aqueous solution. Synchrotron X-ray absorption spectroscopy and X-ray diffraction analysis reveal that interaction between ZnO NPs and phosphate induced the transformation of ZnO into zinc phosphate. Transmission electronic microscopy observation shows that the morphology of the particles changed from structurally uniform nanosized spherical to anomalous and porous material containing mixed amorphous and crystalline phases of ZnO and zinc phosphate in the presence of phosphate. To our knowledge, this is the first study in which the detailed process of phosphate-induced speciation and microstructural transformation of ZnO NPs has been analyzed. In view of the wide existence of phosphate contamination in water and its strong metal-complexation capability, phosphate-induced transformations may play an important role in the behaviors, fate, and toxicity of many other metal-based nanomaterials in the environment.

INTRODUCTION

Because of the large quantities produced and their widespread application, manufactured nanoparticles (NPs) will inevitably enter the environment and it is estimated that their release to the environment will increase drastically in the near future.¹ ZnO NPs are a common type of engineered nanomaterials that have been widely used in many applications such as sunscreen products, textiles, paintings, industrial coatings, and antibacterial agents.² They are consequently released into the environment at volumes reported to be second only to TiO_2 NPs.³ The potential environmental implications of ZnO NPs have recently led to increasing concern. Studies have demonstrated the potential toxicity of nano-ZnO to mammals, bacteria, plants, and phytoplankton^{4–6} and have attributed their toxicity to both the NPs and the dissolved Zn ions.

Due to their high reactivity, it is unlikely that engineered NPs will remain in their original form after release into the environment. Environmental components will inevitably interact with NPs and influence their physicochemical properties and microstructure and consequently determine their potential toxicity and fate in the environment.^{7,8} Only a few studies have addressed the influence of environmental factors

such as aqueous pH and ionic strength and nanoparticle size on the behavior of NPs in the environment.^{9–12} Some recent studies have also investigated interactions between NPs and natural organic matter (NOM), taking into consideration their ubiquity in the environment together with their high reactivity,¹³ and the results have shown that dissolved NOM can enhance the stability and dissolution of NPs in water.^{14,15} Nevertheless, we are still far from understanding the influence of environmental factors on the behavior of NPs in the natural environment. Many other important components such as phosphates are also present in addition to NOM, and these may interact with NPs and affect their behavior and fate.^{17,18} In addition, significant progress has been made in understanding the physicochemical properties (e.g., stability, aggregation, dissolution, and surface chemistry) of NPs.^{19–22} However, very few studies have focused on the speciation and microstructural

Received: March 15, 2012

Revised: May 29, 2012

Accepted: May 31, 2012

Published: May 31, 2012

transformation of NPs under natural environmental conditions.^{23,24}

Phosphates are a major source of contamination in water. Application of phosphate fertilizers has released large amounts of phosphate into surface and underground waters.²⁵ Municipal waste waters and industrial effluents usually contain large amounts of phosphate and have a high potential to release phosphate into the environment. Therefore, interaction between NPs and phosphate in the natural aqueous environment is inevitable. Metal oxide NPs have high specific surface area and are more reactive than ordinary-sized particles.²⁶ Therefore, phosphate would be expected to have great potential to interact with metal oxide NPs and to influence their speciation and microstructure in the environment. However, to the best of our knowledge, there have been no reported studies on how phosphate influences the transformation of speciation or microstructure of any type of NPs.

Moreover, phosphate is an essential component of many culture media used in the toxicity testing of NPs. However, studies on nanotoxicity have paid little attention to the influence of medium components on the properties or toxicity of NPs.²⁷ Li et al.²⁸ recently investigated the influence of medium components on the toxicity of ZnO NPs to *Escherichia coli* and found that phosphate in buffer solution dramatically decreased the concentration of Zn^{2+} ions, resulting in lower toxicity. This study suggests a significant impact of phosphate on the toxicity of ZnO NPs. Unfortunately, the potentially important influence of phosphate on dissolution and transformation of speciation and microstructure of ZnO NPs was not discussed due to the specific focus of the research. Detailed understanding of the influence of phosphate in culture media on the dissolution and transformation of speciation and microstructure of NPs is imperative to avoid erroneous estimates of their toxicity.

In the present study we sought to determine how phosphate influences the dissolution and transformation of ZnO NPs. An attempt was made for the first time to characterize the speciation and microstructure and quantify the transformation process of ZnO NPs using a combination of comprehensive analytical techniques, namely X-ray diffraction (XRD), high-resolution transmission electronic microscopy (HRTEM), and synchrotron-based extended X-ray absorption fine structure spectroscopy (EXAFS), to analyze the microstructure of the reaction products generated. The results of this study are expected to help better understand the fate of ZnO NPs in the natural environment.

MATERIALS AND METHODS

Characterization of ZnO NPs. The ZnO NPs were purchased from Nachen Science & Technology Co., Beijing, China, with a purity of 99.9%. The ζ potentials of ZnO NPs were measured at different pH values over the range of pH 6.5–11 in 0.01 M NaNO_3 solution with a Malvern Nano ZS (Malvern Instruments, UK). Transmission electron microscope (TEM) analysis was carried out with an H-9000NAR (Hitachi, Japan) at 300 kV, and samples were prepared by loading 10- μL aliquots of ZnO NPs or reaction samples onto a carbon-coated grid sample holder. Aggregation and sedimentation of ZnO NPs were examined using time-resolved dynamic light scattering by Malvern Nano ZS (Malvern Instruments, UK) and time-resolved optical absorbency at 378 nm using a UV-vis spectrophotometer (UV759S, Shanghai, China), respectively.¹⁹ The specific surface areas of selected samples were

calculated from N_2 sorption isotherms by the Brunauer–Emmett–Teller (BET) method using N_2 absorption apparatus (Micromeritics ASPA 2010).

Reaction of ZnO NPs with Phosphate. ZnO NPs (containing 10 mM Zn) were mixed in a 10 mM NaNO_3 solution with varying concentrations of K_2HPO_4 to obtain P/Zn molar ratios of 0, 0.2, 0.5, and 1.0 with the pH adjusted to 7.0 ± 0.2 using 0.1 M HNO_3 and NaOH. Mixed suspensions (2 L) were shaken at 100 rpm at room temperature for 15 days. A 20-mL fraction was removed as a reaction sample at different time intervals. Dissolved Zn^{2+} and nanoparticles were separated by centrifugation at 20 000g for 40 min²⁹ and the supernatants were filtered using suction filtration with a 0.025- μm micro-porous membrane (Millipore). A drop of filtrate was placed on a TEM grid for analysis to determine the possible presence of nanoparticles in filtrates, and there were no ZnO NPs detected in the filtrates, confirming the reliability of separation. The filtrates were then acidified with 100 μL of HNO_3 for the determination of Zn and P. The residue was washed three times with deionized water and lyophilized using a freeze-dryer (Labconco, FreeZone 2.5) at -40°C and 0.13 m Bar pressure for 12 h. In similar conditions, varying concentrations of K_2HPO_4 were added to 30 mL of ZnO NP suspension (containing 10 mM Zn) to obtain the desired P/Zn molar ratios from 0 to 4.0 (actual P/Zn molar ratios are provided in Table S1). After shaking for 24 h, samples were centrifuged, filtered, and analyzed, and the residues were washed and lyophilized using the method described above. In addition, 0.0010 g of dry residues were accurately weighed, dissolved in 1 mL of HNO_3 , and then diluted with deionized water to 10 mL for the determination of Zn and P contents in the solid phase. Concentrations of Zn and P were quantified by ICP-MS (Agilent, 7500a) and ICP-OES (Perkin-Elmer, OPTIMA 2000DV), respectively. All the batch experiments were carried out in triplicate.

Structural Characterization of ZnO NPs. Lyophilized powder samples were coated homogeneously on Kapton tapes for X-ray absorption spectroscopy (XAS) analysis. Zinc K-edge (9659 eV) XAS spectra were collected at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (Beijing, China) and beamline 14W at the Shanghai Synchrotron Radiation Facility. ZnO NPs, $\text{Zn}(\text{OH})_2$, hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) powders, and aqueous ZnSO_4 solution (representing Zn^{2+}) were used as reference compounds. $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ exists in two crystal structures, orthorhombic hopeite and triclinic parahopeite. However, differences between the Zn K-edge XAS spectra of the two structures cannot be distinguished (refer to detailed explanation in Supporting Information). Therefore, only hopeite was used as the reference compound of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. An energy range of -200 – 1000 eV from the K-edge of Zn (9659 eV) was used in EXAFS data collection. All sample and reference compounds (except ZnSO_4 solution) data were collected in transmission mode. Standard EXAFS data reduction procedures were undertaken using the program package IFEFFIT.³⁰ X-ray diffraction (XRD) analysis of ZnO NPs and reaction samples was performed in reflection mode on an X'Pert PRO MPD (PANalytical) diffractometer using a $\text{CuK}\alpha$ ($\lambda = 0.154$ nm) radiation in the 2θ scanning range of 5 – 80° . The XRD patterns were refined according to the Rietveld method with the material analysis using the diffraction (MAUD) program package.^{31,32}

Figure 1. Concentration of dissolved Zn²⁺ (A) and P in solution (B) as a function of time with four different P/Zn molar ratios; concentration of dissolved Zn²⁺ (C) and the amount of P loss (ΔC_p) in solution (D) as a function of P/Zn molar ratio ranging from 0 to 4.0 in 24 h (initial ZnO NP content was 10 mM in 0.01 M NaNO₃ at pH 7.0). Each value represents the mean of three replicates with standard deviation shown by error bars.

Figure 2. Contents of P and Zn in solid phase (mmol g⁻¹) as a function of P/Zn molar ratio (A) (arrows point to related axis), and the proportion of P adsorbed and precipitated in solid phase at different P/Zn molar ratios (B). Each value represents the mean of three replicates with standard deviation shown by error bars.

RESULTS AND DISCUSSION

Dissolution of ZnO NPs in the Presence of Phosphate.

ZnO NPs used in this study were mainly spherical in shape with an average particle size of 40 ± 11 nm (size distribution is provided in Figure S1 in Supporting Information) obtained by measuring about 200 single nanoparticles. The isoelectric point (IEP) of ZnO NPs was 9.1, indicative of positive surface charges at pH < 9.1. The ZnO NPs were poorly dispersed and readily aggregated to 450–800 nm within 4 h in solution (Figure S1 in the Supporting Information).

First, the influence of phosphate on the dissolution of ZnO NPs was investigated. The kinetic dissolution study of ZnO NPs at different P/Zn molar ratios in 10 mM NaNO₃ solution was performed with an initial pH of 7.0 ± 0.2 without further adjustment, and the final pH value increased by 0.1–0.3 units. In the absence of phosphate, ZnO NPs dissolved rapidly within the first 3 h and reached equilibrium within 12 h with a dissolved Zn²⁺ concentration of 10.68 mg L⁻¹ (release proportion 1.6%). In the presence of phosphate with a P/Zn molar ratio of 0.2 and 0.5, the concentration of dissolved Zn²⁺ increased with time and reached a plateau after about 72 h with a final dissolved Zn²⁺ concentration of 0.84 and 0.22 mg L⁻¹ (release proportion 0.13 and 0.034%), respectively (Figure 1A).

However, at a P/Zn molar ratio of 1.0, the Zn²⁺ concentration decreased slowly over time with a minimum dissolved Zn²⁺ concentration of only 0.06 mg L⁻¹ in solution (release proportion 0.01%). The concentration of P in solution was also measured (Figure 1B) and displayed a similar pattern of change for the three different P/Zn molar ratios. It decreased dramatically during the first 3 h followed by a continuously slower decline. A rapid Zn²⁺ release from ZnO NPs in the absence of phosphate occurred during the first 3 h and a significant reduction in P concentration in solution also occurred during this period. It is therefore expected that a rapid sequestration reaction might take place between Zn²⁺ and PO₄³⁻, causing the reduction in Zn²⁺ and P in solution.

Figure 1C shows the released Zn²⁺ from ZnO NPs with increasing P/Zn molar ratio ranging from 0 to 4.0 in solution. The concentration of dissolved Zn²⁺ decreased sharply when the P/Zn molar ratio increased from 0 to 0.5 followed by a slight increase when the P/Zn molar ratio increased from 0.7 to 4.0. The loss of P in solution increased rapidly when the P/Zn molar ratio increased from 0 to 2.0 and then slowly from a ratio of 2.0 to 4.0 (Figure 1D), which was very different from the change in Zn²⁺ concentration in solution. This observation suggests that, except for a rapid reaction with Zn²⁺ in solution,

Figure 3. Experimental k space Zn K edge EXAFS spectra (line) and LCF (dot) of the P/Zn (A) and time (C) dependent reaction samples; and the percentages of ZnO and hopeite obtained from LCF of the k space EXAFS spectra of the P/Zn (B) and time (D) dependent reaction samples.

Figure 4. Experimental XRD spectra of the time (A) and P/Zn (C) dependent reaction samples, and proportions of three crystal phases (zincite, hopeite, and parahopeite) in time (B) and P/Zn (D) dependent reaction samples obtained by XRD refinement analysis.

PO_4^{3-} might react on solid phase surfaces by adsorption and precipitation. The contents of Zn and P in the solid phase were therefore measured. Opposite trends exist for the contents of Zn and P in the solid phase with increasing P content from 0 to 3.0 mmol g^{-1} and decreasing Zn content from 11.2 to 7.7 mmol g^{-1} (Figure 2A). The amount of P sequestered in solid phase was much lower than the loss of P in solution, likely attributable to the loosely surface-adsorbed PO_4^{3-} which was subsequently removed with washing. The proportions of the adsorbed and precipitated P were obtained and characterized by an increase in P adsorption and a decrease in P precipitation with increasing P/Zn molar ratio (Figure 2B), implying that sequestration was the preferred reaction between Zn^{2+} and PO_4^{3-} at lower P concentrations and adsorption of PO_4^{3-} was

more obvious at higher P concentrations. All the information indicates that, in the presence of phosphate, reactions such as Zn^{2+} release from ZnO NPs and adsorption and precipitation of PO_4^{3-} should take place and induced a complex component and structural transformation of ZnO NPs.

Synchrotron XAS Analysis of the Transformation Products of ZnO NPs. Synchrotron radiation Zn K-edge XAS is sensitive to the local environment around the center Zn atom in both ordered and disordered structure; information obtained from XAS spectra is therefore a combination of the results of crystalline and amorphous phases together.³³ The Zn K-edge X-ray near edge structure (XANES) spectra with detailed analysis of all the reaction samples and reference compounds are provided in Figure S2 in the Supporting

Figure 5. TEM image of the pristine ZnO NPs (A) and the reaction samples with P/Zn molar ratio of 0.1 (B) and 1.0 (C) for 24 h treatments; and HRTEM images of areas pointed by arrow 1 (E), arrow 2 (F), and arrow 3 (G).

Information. The diagnostic feature of Zn K-edge XANES spectra of the reaction samples was clearly transformed from ZnO with a structure of ZnO_4 tetrahedron to hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) containing both ZnO_4 tetrahedron and ZnO_6 octahedron with increasing P/Zn molar ratio and time. Quantitative analysis of the component proportion in the reaction samples was performed by linear combination fitting (LCF) of the k space of Zn K edge EXAFS spectra (Figure 3A) using ZnO and hopeite as reference compounds. The LCF results are shown in Figure 3B. Losses of solid phase were neglected because the Zn^{2+} release proportion was below 1.6%. The proportion of zinc phosphate in the samples increased from 8 to 73% with increasing P/Zn molar ratio from 0.1 to 4.0. Assuming that the transformation product was $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, the proportion of ZnO and $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ can be calculated from the P and Zn contents in the solid phase (Figure 2B). Details of the calculation are given in the Supporting Information and the results are shown in Figure S3. The results were highly consistent with the XAS-LCF results, which further supports $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ as the transformation product.

Zn K-edge XAS spectra of the reaction products of ZnO NPs with phosphate at a P/Zn molar ratio of 1.0 at different times were also analyzed. There was a clear difference in XANES spectra between the pristine ZnO NPs and the reaction samples during the first 3 h (Figure S2B in the Supporting Information), indicating a rapid reaction between ZnO NPs and phosphate. Zn K-edge k space EXAFS spectra and LCF results of the kinetic reaction products (Figure 3C and D) reveal that the proportion of zinc phosphate increased from 59 to 93% with increasing reaction time from 3 h to 15 days, indicating that within the first 3 h and 15 days up to about 60% and over 90% of ZnO NPs were transformed into zinc phosphate, respectively. This suggests that the presence of phosphate may influence the lifetime of ZnO NPs in the aqueous environment.

XRD Analysis of Transformation Products of ZnO NPs.

XRD analysis was used to further verify whether there was crystalline transformation of ZnO NPs in the presence of

phosphate since XRD is only quantitative for crystalline phases but not for amorphous phases.²⁴ The XRD data of the time and P/Zn dependent reaction products are shown in Figure 4A and C. Three main crystalline phases, hexagonal zincite (ZnO , PDF 35-1451), orthorhombic hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, PDF 33-1474), and triclinic parahopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, PDF 39-1352), were found using the Jade XRD pattern processing software.³⁴ Hopeite and parahopeite have the same chemical formula, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, but have different crystal structures, orthorhombic and triclinic crystals, respectively. The intensity of the peaks related to zincite appeared to decrease while those of hopeite and parahopeite clearly increased with an increase in either reaction time or phosphate content (Figure 4).

To quantify the proportions of the three crystal phases, Rietveld refinement analysis of the reaction samples was performed (an analysis example is provided in Figure S4 in Supporting Information). The changes in phase proportion obtained by refinements (Figure 4B and D) show that crystalline phase transformation from zincite to zinc phosphate including hopeite and parahopeite occurred rapidly. Within the first 3 h about 64% of crystalline zincite was transformed to zinc phosphate and about 99% of crystalline zincite was converted to zinc phosphate at the end of 15 d. When the P/Zn molar ratio increased from 0.1 to 4.0, the proportion of crystalline zincite decreased from 75 to 21%. A clear crystalline phase transformation was observed when the P/Zn molar ratio changed from 0.1 to 1.0, and the changes in phase proportion were then not obvious at a P/Zn molar ratio >1.0 , indicating that once the phosphate concentration exceeded $2/3$ of ZnO NPs, the dosage effect on the crystalline phase transformation almost disappeared. About equal proportions of hopeite and parahopeite were obtained in the crystalline phase zinc phosphate with the exception of the products for P/Zn molar ratios <0.5 , in which the proportion of hopeite was much higher than that of parahopeite and the relative ratio of crystalline parahopeite to hopeite increased with increasing P/Zn molar ratio from 0.1 to 0.5. It is speculated that crystalline hopeite formed preferentially at phosphate concentrations below the stoichiometric P/Zn molar ratio of $2/3$, possibly

due to their different spatial structure. Above all, the XRD results reveal a clear P/Zn ratio and time-dependent crystalline phase transformation from zincite to zinc phosphate.

Morphology of the Transformation Products of ZnO NPs. To obtain more detailed and solid evidence of morphological change of ZnO NPs affected by phosphate, pristine ZnO NPs and reaction samples with P/Zn molar ratios of 0.1 and 1 for 24 h were recorded by TEM and HRTEM, and their specific surface areas were analyzed. TEM images show that the pristine ZnO NPs were spherical (Figure 5A) with a particle size range of 30–50 nm. Clear morphological change was observed in the reaction samples. When the P/Zn molar ratio was 0.1, the boundaries of the particles became amphibolous and larger aggregates were present (Figure 5B), indicative of corrosion damage on the NP surfaces. Accordingly, the surface areas of the samples reduced to $9 \pm 1 \text{ m}^2 \text{ g}^{-1}$ from the surface area of pristine ZnO NPs ($27 \pm 1 \text{ m}^2 \text{ g}^{-1}$). When the P/Zn molar ratio increased to 1.0, spherical nanoparticles almost disappeared and anomalous porous particles of much larger size were present (Figure 5C). As the result of the formation of nanoporous structures, the surface areas of the samples increased to $40 \pm 2 \text{ m}^2 \text{ g}^{-1}$, much larger than the pristine ZnO NPs.

The HRTEM image of single ZnO NP (Figure 5D) further showed a clear crystal lattice, indicative of a highly crystalline structure. The interplanar distance was measured to be 0.280 nm, corresponding to the (100) plane of hexagonal ZnO (2.8 Å).³⁵ However, the HRTEM images of the selected areas of the reaction sample with a P/Zn molar ratio of 1.0 show that the crystalline structures of the particles were poor and not uniform. Grains with different lattice fringes representing orthorhombic hopeite and triclinic parahopeite were observed (Figure 5E, F), in agreement with the XAS and XRD results. A detailed discussion is provided in the Supporting Information. In addition, the marked areas 4, 5, 6 (enlarged in Figure S5) showed no distinct crystal lattice, implying the generation of amorphous matrices present on the edge of the particles and the interstices of grains. The combination of HRTEM and XRD analysis indicates that the transformation products of ZnO NPs were composed of crystalline hopeite, parahopeite, and zincite with sufficient amorphous matrices around the crystal phases, possibly as intermediates generated in the transformation process.

Transformation Process of ZnO NPs. As mentioned above, the proportions of ZnO and zinc phosphate obtained by EXAFS and XRD analysis represent the total and crystalline phases, respectively. Therefore, changes in the respective proportions of the total and crystalline phases ZnO and zinc phosphate were obtained (Figure S6). The presence of differences between the total and the crystalline phases implies the existence of amorphous ZnO and zinc phosphate in the transformation process of ZnO NPs, as also observed in the HRTEM images. The amorphous ZnO was considered to be an amorphous $\text{Zn}(\text{OH})_2$ coating formed via hydrolysis of ZnO.¹⁵ This amorphous $\text{Zn}(\text{OH})_2$ was slightly soluble and Zn^{2+} ions were released into solution.¹² Aqueous PO_4^{3-} can be adsorbed on the hydroxylation surface via exchange with OH^- , forming an amorphous Zn phosphate layer. At the same time, dissolved Zn^{2+} was complexed with aqueous PO_4^{3-} , resulting in the formation of amorphous zinc phosphate hydrate precipitate, which was then crystallized along with grain growth. The formation of zinc phosphate hydrate precipitate reduced the free Zn^{2+} ions in solution and therefore promoted the release of

Zn^{2+} ions from ZnO NPs to reach a new equilibrium. Because of the small size of ZnO NPs, phosphatization surface coating could not protect the core of NPs from corrosion, and resulted in a continuous dissolution of ZnO NPs. The solubility, morphology, component, and microstructure of ZnO NPs therefore changed gradually during the whole process (shown in the TOC and Abstract Art).

Environmental Implications. The findings of this work have significant environmental implications. Since the size of the phosphate-induced transformation products of ZnO NPs was much larger than that of the pristine ZnO NPs and few Zn^{2+} ions were released, the toxicity of ZnO NPs (which is considered mainly due to dissolved Zn ions and nanosize effects²⁸) would be greatly reduced. Therefore, it is important to take into account the presence and concentration of phosphate in the surrounding environment when evaluating the toxicity of ZnO NPs. Furthermore, phosphate-induced transformation products in the aqueous environment have larger surface areas and more adsorption sites than the pristine ZnO NPs, and their adsorption capacity for environmental contaminants such as heavy metals and organic contaminants may be stronger compared with the pristine ZnO NPs, thereby influencing the behavior and fate of contaminants. Dissolution is a common property for many metal-based engineered nanomaterials such as Ag, CuO, and CdSe,^{8,36–39} and due to the strong complexing capability of phosphate with heavy metals such as Ag, Cu, and Cd, it is speculated that the potential effects of phosphate on speciation and microstructure transformation are also expected to be usable for many other metal-based NPs. Considering the complexity of environmental components, attention also needs to be paid to the competing transformation process of ZnO NPs with the presence of some other competing ligands such as sulfide.

■ ASSOCIATED CONTENT

● Supporting Information

Additional figures and details on the analyses of Zn K-edge XANES spectra, the crystalline structure transformations observed by HRTEM, and the proportion of ZnO in the solid phase. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86-10-62849683; fax: +86-10-62923563; e-mail: szzhang@rcees.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (Projects 212771-- and 20921063) and the National Basic Research Program of China (Project 2011CB936001).

■ REFERENCES

- (1) Wiesner, M. R.; Lowry, G. V.; Alvarez, P.; Dionysiou, D.; Biswas, P. Assessing the risks of manufactured nanomaterials. *Environ. Sci. Technol.* **2006**, *40* (14), 4336–4345.
- (2) Wu, B.; Wang, Y.; Lee, Y. H.; Horst, A.; Wang, Z. P.; Chen, D. R.; Sureshkumar, R.; Tang, Y. J. J. Comparative eco-toxicities of nano-ZnO particles under aquatic and aerosol exposure modes. *Environ. Sci. Technol.* **2010**, *44* (4), 1484–1489.

- (3) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, Fullerenes) for different regions. *Environ. Sci. Technol.* **2009**, *43* (24), 9216–9222.
- (4) Xia, T.; Kovochich, M.; Liong, M.; Madler, L.; Gilbert, B.; Shi, H. B.; Yeh, J. I.; Zink, J. I.; Nel, A. E. Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties. *ACS Nano* **2008**, *2* (10), 2121–2134.
- (5) Franklin, N. M.; Rogers, N. J.; Apte, S. C.; Batley, G. E.; Gadd, G. E.; Casey, P. S. Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl₂ to a freshwater microalga (*Pseudokirchneriella subcapitata*): The importance of particle solubility. *Environ. Sci. Technol.* **2007**, *41* (24), 8484–8490.
- (6) Lin, D. H.; Xing, B. S. Phytotoxicity of nanoparticles: Inhibition of seed germination and root growth. *Environ. Pollut.* **2007**, *150* (2), 243–250.
- (7) Lowry, G. V.; Casman, E. A. Nanomaterial transport, transformation, and fate in the environment a risk-based perspective on research needs. *NATO Sci. Peace Secur.* **2009**, 125–137.
- (8) Klaine, S. J.; Alvarez, P. J. J.; Batley, G. E.; Fernandes, T. F.; Handy, R. D.; Lyon, D. Y.; Mahendra, S.; McLaughlin, M. J.; Lead, J. R. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* **2008**, *27* (9), 1825–1851.
- (9) Mudunkotuwa, I. A.; Grassian, V. H. Citric Acid Adsorption on TiO₂ nanoparticles in aqueous suspensions at acidic and circumneutral pH: Surface coverage, surface speciation, and its impact on nanoparticle-nanoparticle interactions. *J. Am. Chem. Soc.* **2010**, *132* (42), 14986–14994.
- (10) French, R. A.; Jacobson, A. R.; Kim, B.; Isley, S. L.; Penn, R. L.; Baveye, P. C. Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles. *Environ. Sci. Technol.* **2009**, *43* (5), 1354–1359.
- (11) Keller, A. A.; Wang, H. T.; Zhou, D. X.; Lenihan, H. S.; Cherr, G.; Cardinale, B. J.; Miller, R.; Ji, Z. X. Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environ. Sci. Technol.* **2010**, *44* (6), 1962–1967.
- (12) Bian, S. W.; Mudunkotuwa, I. A.; Rupasinghe, T.; Grassian, V. H. Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: Influence of pH, ionic strength, size, and adsorption of humic acid. *Langmuir* **2011**, *27* (10), 6059–6068.
- (13) Yang, K.; Lin, D. H.; Xing, B. S. Interactions of humic acid with nanosized inorganic oxides. *Langmuir* **2009**, *25* (6), 3571–3576.
- (14) Zhang, Y.; Chen, Y. S.; Westerhoff, P.; Crittenden, J. Impact of natural organic matter and divalent cations on the stability of aqueous nanoparticles. *Water Res.* **2009**, *43* (17), 4249–4257.
- (15) Mudunkotuwa, I. A.; Rupasinghe, T.; Wu, C. M.; Grassian, V. H. Dissolution of ZnO nanoparticles at circumneutral pH: A study of size effects in the presence and absence of citric acid. *Langmuir* **2012**, *28* (1), 396–403.
- (16) Aiken, G. R.; Hsu-Kim, H.; Ryan, J. N. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. *Environ. Sci. Technol.* **2011**, *45* (8), 3196–3201.
- (17) Phenrat, T.; Saleh, N.; Sirk, K.; Kim, H. J.; Tilton, R. D.; Lowry, G. V. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J. Nanopart. Res.* **2008**, *10* (5), 795–814.
- (18) Dange, C.; Phan, T. N. T.; Andre, V.; Rieger, J.; Persello, J.; Foissy, A. Adsorption mechanism and dispersion efficiency of three anionic additives [poly(acrylic acid), poly(styrene sulfonate) and HEDP] on zinc oxide. *J. Colloid Interface Sci.* **2007**, *315* (1), 107–115.
- (19) Zhou, D. X.; Keller, A. A. Role of morphology in the aggregation kinetics of ZnO nanoparticles. *Water Res.* **2010**, *44* (9), 2948–2956.
- (20) Peukert, W.; Segets, D.; Gradl, J.; Taylor, R. K.; Vassilev, V. Analysis of optical absorbance spectra for the determination of ZnO nanoparticle size distribution, solubility, and surface energy. *ACS Nano* **2009**, *3* (7), 1703–1710.
- (21) Zhang, W.; Yao, Y.; Sullivan, N.; Chen, Y. S. Modeling the primary size effects of citrate-coated silver nanoparticles on their ion release kinetics. *Environ. Sci. Technol.* **2011**, *45* (10), 4422–4428.
- (22) Mudunkotuwa, I. A.; Pettibone, J. M.; Grassian, V. H. Environmental implications of nanoparticle aging in the processing and fate of copper-based nanomaterials. *Environ. Sci. Technol.* **2012**, *46*, No. 10.1021/es203851d.
- (23) Scheckel, K. G.; Luxton, T. P.; El Badawy, A. M.; Impellitteri, C. A.; Tolaymat, T. M. Synchrotron speciation of silver and zinc oxide nanoparticles aged in a Kaolin suspension. *Environ. Sci. Technol.* **2010**, *44* (4), 1307–1312.
- (24) Levard, C.; Reinsch, B. C.; Michel, F. M.; Oumahi, C.; Lowry, G. V.; Brown, G. E. Sulfidation processes of PVP-coated silver nanoparticles in aqueous solution: Impact on dissolution rate. *Environ. Sci. Technol.* **2011**, *45* (12), 5260–5266.
- (25) Jaisi, D. P.; Kukkadapu, R. K.; Stout, L. M.; Varga, T.; Blake, R. E. Biotic and abiotic pathways of phosphorus cycling in minerals and sediments: Insights from oxygen isotope ratios in phosphate. *Environ. Sci. Technol.* **2011**, *45* (15), 6254–6261.
- (26) Auffan, M.; Rose, J.; Bottero, J. Y.; Lowry, G. V.; Jolivet, J. P.; Wiesner, M. R. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nat. Nanotechnol.* **2009**, *4* (10), 634–641.
- (27) Li, M. H.; Pokhrel, S.; Jin, X.; Madler, L.; Damoiseaux, R.; Hoek, E. M. V. Stability, bioavailability, and bacterial toxicity of ZnO and iron-doped ZnO nanoparticles in aquatic media. *Environ. Sci. Technol.* **2011**, *45* (2), 755–761.
- (28) Li, M.; Zhu, L. Z.; Lin, D. H. Toxicity of ZnO nanoparticles to *Escherichia coli*: Mechanism and the influence of medium components. *Environ. Sci. Technol.* **2011**, *45* (5), 1977–1983.
- (29) Xia, T. A.; Zhao, Y.; Sager, T.; George, S.; Pokhrel, S.; Li, N.; Schoenfeld, D.; Meng, H. A.; Lin, S. J.; Wang, X. A.; Wang, M. Y.; Ji, Z. X.; Zink, J. I.; Madler, L.; Castranova, V.; Lin, S.; Nel, A. E. Decreased dissolution of ZnO by iron doping yields nanoparticles with reduced toxicity in the rodent lung and zebrafish embryos. *ACS Nano* **2011**, *5* (2), 1223–1235.
- (30) Newville, M. IFEFFIT: interactive XAFS analysis and FEFF fitting. *J. Synchrotron Radiat.* **2001**, *8*, 322–324.
- (31) Ferrari, M.; Lutterotti, L. Method for the simultaneous determination of anisotropic residual-stresses and texture by X-ray-diffraction. *J. Appl. Phys.* **1994**, *76* (11), 7246–7255.
- (32) Lutterotti, L. Total pattern fitting for the combined size-strain-stress-texture determination in thin film diffraction. *Nucl. Instrum. Meth. B* **2010**, *268* (3–4), 334–340.
- (33) Waychunas, G. A.; Fuller, C. C.; Davis, J. A. Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine structure spectroscopy analysis. *Geochim. Cosmochim. Acta* **2002**, *66* (7), 1119–1137.
- (34) Materials Data, Inc. Computer software JADE, XRD pattern and processing & identification, version 3.1.
- (35) Tian, Z. R. R.; Voigt, J. A.; Liu, J.; McKenzie, B.; McDermott, M. J.; Rodriguez, M. A.; Konishi, H.; Xu, H. F. Complex and oriented ZnO nanostructures. *Nat. Mater.* **2003**, *2* (12), 821–826.
- (36) Li, X.; Lenhart, J. J. Aggregation and dissolution of silver nanoparticles in natural surface water. *Environ. Sci. Technol.* **2012**, *46* (10), 5378–5386.
- (37) Vogelsberger, W.; Schmidt, J.; Roelofs, F. Dissolution kinetics of oxidic nanoparticles: The observation of an unusual behaviour. *Colloids Surf., A* **2008**, *324* (1–3), 51–57.
- (38) Silk, W. K.; Shi, J. Y.; Abid, A. D.; Kennedy, I. M.; Hristova, K. R. To duckweeds (*Landoltia punctata*), nanoparticulate copper oxide is more inhibitory than the soluble copper in the bulk solution. *Environ. Pollut.* **2011**, *159* (5), 1277–1282.
- (39) Domingos, R. F.; Simon, D. F.; Hauser, C.; Wilkinson, K. J. Bioaccumulation and effects of CdTe/CdS quantum dots on *Chlamydomonas reinhardtii* - nanoparticles or the free ions? *Environ. Sci. Technol.* **2011**, *45* (18), 7664–7669.