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

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HIGHLIGHTS

- ZnO NPs undergo chemical transformation in the presence of insoluble phosphate.
- HAP induced the transformation of ZnO NPs to scholizite 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 (PO_4^{3-}) and calcium anion (Ca^{2+}) were released from HAP in aqueous solution, inducing a rapid transformation of about 80% ZnO NPs to scholizite within 4 h. Under neutral or basic conditions (pH 7 and 9) the adsorption of 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.

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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

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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_2 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_4^{2-} and Cl^-) 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_2S) or hydrogen sulfide (H_2S) [12,13]. Our previous research [14] has confirmed that phosphate ions can induce the transformation of ZnO NPs to tetrahydrate $\text{Zn}_3(\text{PO}_4)_2$ 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 $\text{Zn}_3(\text{PO}_4)_2$ 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 $\text{Zn}_3(\text{PO}_4)_2$, ZnS and Zn associated Fe oxy/hydroxides (Zn–FeOOH) were identified in sludge and biosolids generated by wastewater treatment [16,17]. $\text{Zn}_3(\text{PO}_4)_2$ 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 $\text{Zn}_3(\text{PO}_4)_2$ 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^{2+} , Fe^{3+} , Al^{3+} 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 [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, (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 microtopographys of HAP, ZnO NPs and the samples were obtained with H-7500 (Hitachi, Japan) transmission electron microscope (TEM) operated at 80 kV. The ζ potentials of ZnO NPs and HAP were measured at varied pH in 10 mmol L^{-1} NaNO_3 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^{-1} in 10 mmol L^{-1} NaNO_3 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^{2+} were added to reach a concentration of $65.4 \text{ mg Zn L}^{-1}$. 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 $10,000 \times g$ 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 $0.22 \mu\text{m}$ microporous membrane (Millipore), Filtrates were acidified with $100 \mu\text{L}$ HNO_3 , 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, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, ZnSO_4 aqueous solution and Zn^{2+} adsorbed on HAP (Zn_{ads} -HAP) were used as reference compounds. Spectra were collected in transmission mode for the ZnO NPs and $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ powders, and in fluorescence mode for ZnSO_4 aqueous solution, Zn_{ads} -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 $12.5 \text{ \AA}^{-1}$ 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 ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) and scholzite ($\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$) for Zn–O, Zn–Zn and Zn–P associations generated by FEFF 8.2 were fitted to the experimental spectra. An amplitude reduction factor $S^0 = 0.87$ 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 $\pm 10\%$ and R of $\pm 0.01 \text{ \AA}$. X-ray diffraction (XRD) analysis of the samples

Fig. 1. Time dependent changes of the dissolved Zn concentrations (a) and released PO₄³⁻ (b) and Ca²⁺ (c) concentrations in the ZnO NPs/HAP suspension at different initial pH values.

was performed in reflection mode on an X'Pert PRO MPD (PANalytical) diffractometer using a CuK ($\lambda = 0.154$ nm) radiation in the scan range of 5–90° 2 θ .

3. Results and discussion

3.1. Material characterization

ZnO NPs used in this study were bare particles without surface coating. The crystalline phase of ZnO nanoparticles was consistent with zincite by XRD analysis (Fig. S1C). TEM micrograph indicated that the primary ZnO NPs were nearly spherical with diameters of 40 ± 11 nm obtained by measuring over 200 single particles (Fig. S1A and B). Dynamic light scattering analysis showed that ZnO NPs preferred to aggregation, and the average hydrodynamic diameters of ZnO NPs were 835 ± 75 , 836 ± 75 , 998 ± 151 nm at pH 5, 7 and 9, respectively (Fig. S1D). HAP was composed of loose agglomerates of sheet- and needle-like particles in a wide size distribution from few nanometers up to few micrometers (shown in Fig. S2A and B). The XRD patterns of HAP revealed that the crystalline phase was consistent with standard HAP (Fig. S2C). Surface charge was reported to be an important factor to impact the stability of nanoparticle/clay mineral mixtures [26]. The positive surface charge of both ZnO NPs and HAP at pH 5 and 7 implied their negligible electrostatic attraction. At pH 9, electrostatic attraction between ZnO NPs and HAP might promote their heterogeneous aggregate because of the opposite surface charges between ZnO NPs and HAP. The addition of ZnO NPs into HAP suspension did not obviously change the zeta potential of HAP suspension (Fig. S3B).

3.2. Dissolution of ZnO NPs in the presence of HAP

Dissolution of ZnO NPs in the presence of HAP at different initial pH (5.0, 7.0 and 9.0 ± 0.1) was investigated (Fig. 1A). The addition of ZnO NPs increased the suspension pH value for roughly 1 and 0.5 units above the initial pH values of 5.0 and 7.0, respectively, whereas little change was observed for the suspension at pH 9.0. In ZnO NPs/HAP suspension at initial pH 5, the dissolved Zn concentration increased sharply in the first 4 h and then gradually decreased, indicating that dissolution of ZnO was faster than the subsequent Zn²⁺ sequestration. In contrast, the dissolved Zn concentration in the ZnO NPs/HAP suspensions at pH 7 and 9 continued to increase slowly in the first 5 days and then reached a plateau without further change. Over 10 days, a similar Zn²⁺ concentration (0.61 mg L^{-1} with ZnO dissolution rate of about 0.9%) in the suspensions at pH 5 and 7 was obtained, which was slightly higher than Zn²⁺ concentration in the suspension at pH 9 (0.26 mg L^{-1} with ZnO dissolution rate of about 0.4%). The amount of Zn²⁺ released from ZnO NPs was greatly reduced in the presence of HAP (as shown in Fig. S4) irrespective of the initial pH value, indicating that HAP can effectively sequester Zn²⁺ released from ZnO NPs.

To assess the available PO₄³⁻ and Ca²⁺ for the reaction with Zn²⁺, concentrations of PO₄³⁻ and Ca²⁺ were detected (Fig. 1b and c). At

pH 5, the concentrations of PO₄³⁻ and Ca²⁺ in the HAP suspension were about 143 mg L^{-1} and 98 mg L^{-1} prior to the addition of ZnO NPs, and were reduced to about 49 mg L^{-1} and 80 mg L^{-1} after the addition of ZnO NPs, respectively. The reduction in the concentrations of PO₄³⁻ and Ca²⁺ suggested the coprecipitation of Zn²⁺ released from ZnO NPs with PO₄³⁻ and Ca²⁺ at pH 5. We speculated that sequestration of the released Zn²⁺ from solution would induce further dissolution of ZnO NPs and accelerate chemical transformation of ZnO NPs, similar to the role of PO₄³⁻ in sequestering Zn²⁺ released from ZnO NPs [14]. However, HAP only dissolved to a very small extent with PO₄³⁻ concentration detected at 0.67 and 0.75 mg L^{-1} in the ZnO NPs/HAP suspensions at pH 7 and 9, respectively, so that coprecipitation of Zn²⁺ with PO₄³⁻ and Ca²⁺ might be insignificant.

3.3. XRD analysis of ZnO NPs/HAP mixture

The crystalline structure changes of the ZnO NPs/HAP samples were monitored using XRD over the course of 30 days. XRD patterns (Fig. 2) clearly showed a new peak (Fig. 2, solid arrows) and the diagnostic peaks of ZnO in the sample almost disappeared after 4 h of the interaction between ZnO NPs and HAP. However, the diagnostic peaks of ZnO (Fig. 2, dashed arrows) remained and no new peak appeared over the course of the reactions in the samples with pH of 7 and 9. The new crystal phase was identified as scholite crystal [CaZn₂(PO₄)₂·2H₂O] [27], but not (para)hopeite [Zn₃(PO₄)₂·4H₂O] as the transformation product of ZnO NPs induced by phosphate in aqueous solutions [14]. Moreover, the molar ratio of the sequestered contents of PO₄³⁻ and Ca²⁺

Fig. 2. XRD patterns of ZnO NPs interacted with HAP. Solid arrows represent diagnostic peak of scholite, and dashed arrows represent diagnostic peaks of zincite.

Fig. 3. Zn K-edge XANES and radial structural function (RDF) of ZnO NPs interacted with HAP at various times under pH 5 (a, d), 7 (b, e) and 9 (c, f). Black line represents experimental data and red broken line is the line of best fit, H_a and H_b represent H_{Zn-O} and H_{Zn-Zn} , respectively.

in solution was approximately 2:1 in the ZnO NPs/HAP suspension at pH 5, consistent with the P/Ca ratio in the chemical formula of scholite. Therefore, it is reasonable to expect that the formation of scholite was most likely through coprecipitation of Zn^{2+} released from ZnO NPs with PO_4^{3-} and Ca^{2+} released from HAP. The pK_{sp} values for $Zn_3(PO_4)_2$ and scholite were 32.04 and 34.10, respectively [28,18], indicating that scholite was slightly more stable than $Zn_3(PO_4)_2$ and the formation of scholite was more thermodynamically favored than $Zn_3(PO_4)_2$ if there were enough Ca^{2+} ions available. Therefore, dissolution followed by coprecipitation was thought to be the main mechanism responsible for the formation of scholite in the ZnO NPs/HAP suspensions at pH 5. The equilibrium pH would increase with the reactions below, thus decreasing

the dissolution of ZnO and HAP and the subsequent formation of scholite.

No new crystalloid phase was found in the ZnO NPs/HAP suspensions at the initial pH of 7 and 9, possibly due to the low solubility of ZnO NPs and HAP under neutral and alkaline conditions. Rathnayake et al. [15] also observed the formation of amorphous shell of $\text{Zn}_3(\text{PO}_4)_2$ rather than crystalline hopeite at alkaline condition (pH 8). Since XRD is only sensitive to crystalline phases, the possible amorphous products formed following chemical transformation of ZnO NPs are still unknown and warrant further investigation.

3.4. Synchrotron XAFS analysis of ZnO NPs in ZnO NPs/HAP mixture

Synchrotron Zn K-edge XAFS is sensitive to the local structure of the center Zn atom including both crystalline and amorphous phases. There were distinct differences of Zn K-edge XANES features between the samples and ZnO NPs. For the sample with an initial pH of 5, two diagnostic inflexions at 9669.1 eV and 9680.3 eV of ZnO shifted to 9665.2 eV and 9677.9 eV within 4 h (Fig. 3a), respectively, indicating an extreme and rapid change in the Zn coordination environment. This is consistent with the XRD results which showed the crystalline transformation of ZnO from zincite to scholite within 4 h. For the samples with the initial pH values of 7 and 9, similar energy shifts were observed, but with a slower initial rate and lower extent of transformation than that of pH 5 (Fig. 3b and c), suggesting a relatively minor change in Zn coordination.

More accurate information on the changes of the coordination environment of Zn in the samples was obtained using radial distribution functions (RDFs) from the Fourier transform of EXAFS spectra. The crystalloid ZnO was composed of ZnO_4 tetrahedron with regular arrangement, around the center Zn containing 4 Zn–O bonds at 1.97 Å, 12 Zn–Zn bonds at 3.21 Å, and 12 Zn–Zn bonds at 4.55 Å. The features of RDFs (Fig. 3d–f) apparently revealed that the intensities of the first Zn–O shell and the second Zn–Zn shell of ZnO NPs decreased obviously in all the samples with increasing time. The Zn–Zn shell almost disappeared in the samples with an initial pH of 5 and reaction time over 4 h. The disappearance of the Zn–Zn shell indicated the crystalloid long-range order of ZnO was destroyed. This further explained the disappearance of the diagnostic peaks of ZnO in the XRD spectra.

The EXAFS spectra of the phosphatized ZnO NPs samples containing ZnO in a wide range of proportions were obtained in our previous research [14], and the RDFs of EXAFS spectra for the samples are displayed in Fig. S5. There are two linear ranges between the relationship of peak height ratios of the first two shells ($H_{\text{Zn-O}}/H_{\text{Zn-Zn}}$) and ZnO proportions in the samples (as shown in Fig. 4), and two linear equations ($y = -0.066x + 3.883$ and $y = -0.008x + 1.422$, with $R^2 = 0.98$ and 0.92 , respectively) were therefore obtained. Using these two equations the proportions of ZnO in ZnO NPs (ZnO 100%), ZnO NPs/hopeite mixture (ZnO 64%), ZnO NPs/hopeite mixture (ZnO 43%) and hopeite (ZnO 0%) were

Fig. 4. Relationship between the $H_{\text{Zn-O}}/H_{\text{Zn-Zn}}$ values and ZnO proportions.

estimated to be 104%, 63%, 40% and –1%, respectively, confirming that the equations can be used to estimate ZnO proportions in the samples. The ZnO proportions obtained for all the samples are shown in Fig. 5a. In the ZnO NPs/HAP samples with pH of 5, 80% ZnO NPs were transformed to Zn phosphate within 4 h, while the remaining 20% were still persistent at the end of 30 d. In addition, no crystalline zincite was observed in these samples by XRD analysis, suggesting that the remaining 20% ZnO existed mainly in amorphous phases or poorly crystalline phases with small crystal grains that cannot be detected by XRD. In the ZnO NPs/HAP samples with initial pH of 7 and 9, the proportion of ZnO decreased gradually with increasing time, leaving 35% and 40% of ZnO in the samples at the end of 30 days, respectively. However, there was no new crystalloid phase identified by XRD, indicating that the transformed products of ZnO NPs in the ZnO NPs/HAP suspensions at pH 7 and 9 were mainly present in amorphous phase, in good agreement with the results reported previously [15]. At pH 7 and 9, the dissolved phosphate concentration was very low (below 1 mg L^{-1} as shown in Fig. 1), so that transformation of ZnO induced by soluble phosphate was insignificant. Instead, the adsorption of Zn^{2+} released from ZnO NPs on HAP was thought to be the main mechanism of ZnO NPs transformation. Based on this, proportions of components in the ZnO NPs/HAP samples at pH 7 and 9 were quantitatively analyzed with linear combination fitting (LCF) of XANES spectra obtained using ZnO and Zn^{2+} adsorbed on HAP ($\text{Zn}_{\text{ads}}\text{-HAP}$) as reference compounds (Fig. 5b and c). The EXAFS results showed that Zn formed tetrahedral innersphere complexes with 4.1 Zn–O bonds at 1.96 Å and 1.3 Zn–P bonds at 3.40 Å in the samples with pH of 7 and 9 (Table 1), which was consistent with the structure of corner sharing between tetrahedral Zn and PO_4 as previously reported [22]. The reduced proportions of ZnO calculated by LCF were similar to the results estimated by $H_{\text{Zn-O}}/H_{\text{Zn-Zn}}$ ratios (Fig. 5a), further confirming the transformation of ZnO NPs to $\text{Zn}_{\text{ads}}\text{-HAP}$ in the samples with the pH of 7 and 9. Based on the analysis above, we can

Fig. 5. The proportion of ZnO in ZnO NPs/HAP samples under pH 5, 7 and 9 at various times estimated by $H_{\text{Zn-O}}/H_{\text{Zn-Zn}}$ values (a), and the proportion of ZnO and $\text{Zn}_{\text{ads}}\text{-HAP}$ in the samples under pH 7 and 9 calculated by LCF (b, c).

Table 1

Zn K edge EXAFS fit results for model compounds and samples.

	Shell	CN	R (Å)	δ^2 (Å ²)	E_0 (eV)		Shell	CN	R (Å)	δ^2 (Å ²)	E_0 (eV)
Zn ²⁺ (aq)	Zn–O	5.8	2.07	0.007	3.56	HAP, pH 7, 4 h	Zn–O	3.5	1.97	0.004	3.21
ZnO	Zn–O	4.0 ^a	1.97	0.005	4.48	HAP, pH 7, 24 h	Zn–Zn	7.8	3.21	0.009	2.86
	Zn–Zn	12.0 ^a	3.21	0.009			Zn–O	7.8	4.55	0.012 ^a	
	Zn–Zn	12.0 ^a	4.55	0.012			Zn–O	3.7	1.97	0.005	
Zn _{ads} –HAP	Zn–O	4.1	1.96	0.007	0.47		Zn–Zn	5.2	3.26	0.010 ^a	
	Zn–P	1.3	3.40	0.005			Zn–P	2.5	3.32	0.001	
Hopeite	Zn–O	4.1	1.96	0.008	5.75	HAP, pH 7, 30 d	Zn–Zn	5.9	4.56	0.012 ^a	1.50
	Zn–P	1.0	3.09	0.010 ^a			Zn–O	4.0	1.96	0.006	
	Zn–Zn	2.3	3.39	0.010 ^a			Zn–Zn	4.0	3.24	0.010 ^a	
							Zn–P	1.5	3.32	0.001	
HAP, pH5, 4 h	Zn–O	3.8	1.95	0.004	0.90	HAP, pH 9, 4 h	Zn–O	3.5	1.97	0.004	3.17
	Zn–Zn	3.6	3.30	0.010 ^a			Zn–Zn	9.2	3.21	0.009	
	Zn–P	1.2	2.99	0.010 ^a			Zn–Zn	9.7	4.55	0.012 ^a	
HAP, pH5, 24 h	Zn–O	3.7	1.95	0.004	3.78	HAP, pH 9, 24 h	Zn–O	3.6	1.97	0.004	3.55
	Zn–Zn	3.8	3.32	0.010 ^a			Zn–Zn	8.9	3.21	0.010	
	Zn–P	1.4	3.03	0.010 ^a			Zn–Zn	8.8	4.55	0.012 ^a	
HAP, pH5, 30d	Zn–O	3.8	1.95	0.004	0.59	HAP, pH 9, 30 d	Zn–O	3.8	1.97	0.006	0.66
	Zn–Zn	3.8	3.31	0.010 ^a			Zn–Zn	4.1	3.25	0.010 ^a	
	Zn–P	1.6	2.99	0.010 ^a			Zn–P	2.2	3.32	0.002	
							Zn–Zn	4.4	4.53	0.012 ^a	

^a Fixed parameters.

conclude that ZnO NPs were chemical unstable in the presence of HAP under both acidic and basic conditions. The half-life of ZnO NPs in the presence of HAP was estimated to be about 2.5, 28 and 75 h at pH 5, 7 and 9, respectively.

Furthermore, the local structural environment and coordination of zinc in the ZnO NPs/HAP samples were investigated (Fig. 5d–f). The EXAFS fitting structural parameters of reference compounds and samples are present in Table 1. Hopeite consists of ZnO₄ tetrahedron and ZnO₆ octahedron with their ratio at 2:1, while only ZnO₄ tetrahedron exists in scholizite because ZnO₆ is replaced by CaO₆ octahedron [18]. In all the ZnO NPs/HAP samples, there were 3.5–4.1 Zn–O bonds (1.95–1.97 Å) in the first shell, indicating that only ZnO₄ tetrahedron was present. This was consistent with the structure of scholizite but different from that of hopeite. Their XRD pattern also showed there was no hopeite in the samples. Combining the information obtained by EXAFS and XRD, we can conclude that neither crystalloid nor amorphous hopeite was present in the samples. At pH 5, coordination number (CN) of Zn–Zn bonds at 3.30 Å decreased from 12.0 to 3.6 and Zn–Zn bonds (CN = 12) at 4.55 Å disappeared within 4 h. At the same time, Zn–P bonds (CN = 1.2) at 2.99 Å formed without further change, indicating the formation of a stable structure within 4 h at pH 5. In the standard structure of scholizite, there were 4.0 Zn–P bonds at 3.02–3.15 Å and 2.0 Zn–Zn bonds at 3.33 Å in the second shell [18,22]. Evidence of fewer CN of Zn–P bonds and more CN of Zn–Zn bonds presented in the samples suggested that some ZnO NPs were still remained, consistent with the results obtained by the XRD and LCF analyses that about 20% poorly crystalloid or amorphous ZnO remained in the samples at the end of 30 days. For the samples with pH of 7 and 9, Zn–Zn bonds in the second and third shells decreased with increasing time. Nevertheless the third Zn–Zn shell did not disappear within 30 days, confirming the results that the presence of well crystalloid ZnO in the samples obtained with XRD analysis. However, 1.5–2.5 Zn–P shell at 3.32 Å was present in the samples with a decreasing CN of Zn–Zn bonds. The distance of Zn–P bond in the samples with pH of 7 and 9 was much longer than that of the Zn–P bond in scholizite and the sample with pH of 5 (2.99–3.03 Å) and close to the distance of Zn–P bond (3.40 Å) in the Zn_{ads}–HAP,

indicating that transformation of ZnO NPs in the presence of HAP under neutral and basic conditions was attributed to the formation of inner-sphere Zn adsorption complexes at the HAP surface, but not to the formation of scholizite. This conclusion is in agreement with the results obtained from the XRD and LCF analyses.

4. Conclusions

The present study investigated the chemical transformation of ZnO NPs in the presence of HAP. The results showed that HAP induced chemical transformation of ZnO NPs. Under acidic conditions (pH of 5), phosphate and Ca²⁺ released from HAP resulted a rapid transformation of about 80% ZnO NPs to crystalline scholizite within 4 h. Under neutral and basic conditions (pH of 7 and 9), a slower crystalline to amorphous phase transformation of about 60% ZnO NPs within 30 days was achieved by forming inner-sphere Zn adsorption complexes at the HAP surface. Considering the abundance of insoluble phosphate containing minerals such as HAP in the environment and the fact of Zn phosphate as an important and a persistent transformation product of ZnO NPs [16,17], chemical transformations of ZnO NPs induced by phosphate containing minerals plays a significant role in the behavior, fate and toxicity of ZnO NPs in the environment.

Acknowledgments

This work was funded by the National Natural Science Foundation of China (Projects 21277154 and 41023005) and the Open Fund of State Key Laboratory of Pollution Control and Resources Reuse (Project PCRRF13012).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.07.036>

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