Sonochemical Synthesis of Amorphous Zinc Phosphate Nanospheres

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Amorphous zinc phosphate nanospheres were prepared *via* a sonochemical route. Zinc phosphate nanospheres were uniform in shape with an average diameter of 210 nm. The average diameter of nanospheres could be controlled by changing the pH of a precursor solution. This sonochemical method is simple, facile, economical, and environmentally benign. Non-crystalline characteristics of as-prepared zinc phosphate nanospheres were confirmed by X-ray diffraction, transmission electron microscopy, and FT-IR spectroscopy analyses. We believe this technique will be readily adopted in realizing other forms of zinc phosphate nanostructures.

Key Words: Zinc phosphate, Nanosphere, Ultrasound, Sonochemistry

Introduction

The design of nanostructured materials with various shapes has given an impetus to the development of nanoscience and nanotechnology as a key factor in tailoring the physical and chemical properties of nanostructures.[1-4] Thus the shape control of various nanostructured materials has attracted great attention in recent materials chemistry. Zinc phosphate (Zn$_3$(PO$_4$)$_2$) is one of the most important multifunctional materials for potential applications, including environmentally friendly anticorrosive pigments and dental cements due to its low solubility in water/biological environment and biocompatibility.[5,6] In addition, the catalytic properties of zinc phosphate have been investigated in hydrocarbon conversion process, such as dehydration/dehydrogenation of *sec*-butanol and methanol conversion.[7,8]

Since the first report on the synthesis of microporous zinc phosphates,[9] various techniques, including a solid-state reaction[10] and a polyol-mediated approach,[11] have been investigated for the synthesis of monodispersed and nonagglomerated zinc phosphate nanoparticles. A solid-state reaction is a simple room temperature process, but it requires very long reaction time (from several hours to several days) for the fabrication of zinc phosphate nanoparticles.[10,12] Unlike the solid-state reaction, a polyol-mediated approach is a relatively fast route (up to several hours) to the preparation of nonagglomerated zinc phosphate nanoparticles.[11,13,14] However, the polyol-mediated approach requires both a heating system due to the relatively high temperature process (up to 300 °C) and an additional cooling system for refluxing process.

Therefore, the development of a simple and fast route to the growth of zinc phosphate nanostructured materials with various shapes under ambient conditions has remained an important topic of investigation. In recent years, a sonochemical technique has been developed as a promising alternative technique for the synthesis of morphology-controlled inorganic nanostructured materials.[4,15-17] The reason is that this sonochemical technique is a fast, simple, convenient, economical, and environmentally benign process.[18-20] Herein, we report on the selective synthesis of amorphous zinc phosphate nanospheres *via* a facile sonochemical route.

Experimental Section

Amorphous zinc phosphate nanospheres were fabricated in a horn-type reaction vessel using an ultrasonic technique. Zinc phosphate tetrahydrate (Zn$_3$(PO$_4$)$_2$·4H$_2$O, 98%, Junsei) were used as a precursor chemical. For the production of zinc phosphate nanospheres, 0.4582 g zinc phosphate tetrahydrate was dissolved in a mixture of 15 mL ammonia water (28~30 wt%, Kanto) and 85 mL distilled (DI) water at room temperature. Concentrations of zinc phosphate and ammonia were 0.01 and 2.36 M, respectively. The pH of the precursor solution was 12.3. Ultrasonic wave was introduced at an intensity of 39.5 W/cm^2 for 30 min by a sonochemical apparatus (frequency of 20 kHz) under ambient conditions, in order to synthesize amorphous zinc phosphate nanospheres. The zinc phosphate nanosphere-containing solution was filtered with a polycarbonate membrane that had pores of 100 nm in diameter. Zinc phosphate nanospheres were washed with DI water after filtration, and then dried in an oven.
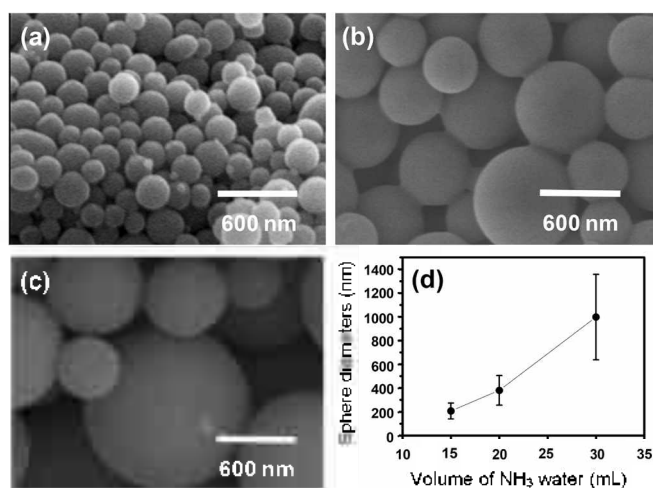
The volumetric ratio between ammonia water and DI water in 100 mL precursor solution was changed for the diameter control of zinc phosphate nanospheres. For large-diametered zinc phosphate nanospheres, the concentration of ammonia was increased to 3.14 M (20 mL ammonia water with 80 mL DI water) and 4.71 M (30 mL ammonia water with 70 mL DI water). The pH of the precursor solution was 12.5 and 12.8 at 3.14 and 4.71 M ammonia concentration, respectively. Except for the difference in ammonia concentration of precursor

solutions, the concentration level of zinc phosphate, an intensity of ultrasonic wave, and reaction time were fixed at 0.01 M, 39.5 W/cm^2, and 30 min, respectively.

The morphology of as-prepared zinc phosphate nanospheres was observed by field emission scanning electron microscope (FESEM, Hitachi S-4300SE). The crystallinity, crystal structure, and chemical composition were characterized by transmission electron microscope (TEM, JEOL JEM-2010), X-ray diffraction (XRD, Max Science, M18XHF), energy-dispersive X-ray (EDX) spectroscopy, and Fourier Transform Infrared (FT-IR) spectroscopy.
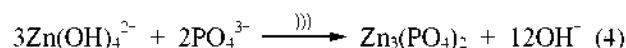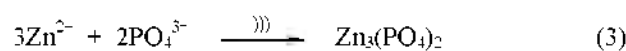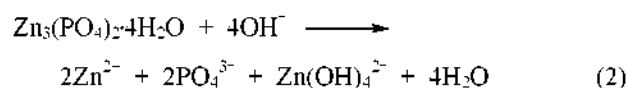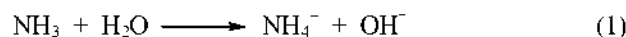
Results and Discussion

Figure 1 shows FESEM images and diameter distribution of as-prepared zinc phosphate nanostructured materials *via* a sonochemical route. Zinc phosphate nanospheres with different diameters could be clearly observed in Figure 1(a)-(c). The average diameter increased from 210 to 1000 nm as the ammonia concentration in precursor solution increased from 2.36 (15 mL in volume, pH = 12.3) to 4.71 M (30 mL in volume, pH = 12.8), as shown in Figure 1(d). At low ammonia concentration of 2.36 M, the standard deviation in diameter was as small as 70 nm. On the contrary, the standard deviation in diameter was as large as 360 nm at high ammonia concentration of 4.71 M. The Ostwald ripening phenomenon is known as a key factor which cause the diameter distribution of nanoparticles by the solubility difference due to size-induced energetic stability.[21,22] Based on Ostwald ripening process, the larger particles continue to grow, while smaller particles continue to shrink. It is thought that, as the ammonia concentration in precursor solution increased from 2.36 to 4.71 M, the Ostwald

ripening phenomenon became enhanced due to the increase in the amount of excessive hydroxyl ions (OH$^-$ ions) which can dissolve zinc phosphate nanospheres. When ammonia water is used as hydroxide anion source material, large amount of growth units can be generated. Thus, isotropic growth from center nuclei can be mainly proceeded to form sphere-like zinc phosphate nanostructures.
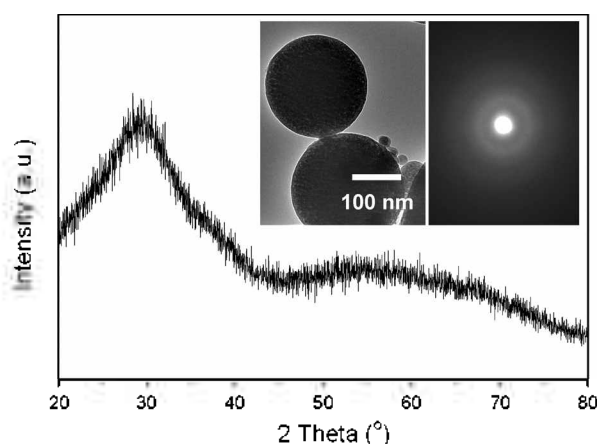
The growth mechanism of zinc phosphate nanospheres was considered as follows:[23]

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \tag{1}$$

$$Zn_3(PO_4)_2 \cdot 4H_2O + 4OH^- \longrightarrow$$
$$2Zn^{2+} + 2PO_4^{3-} + Zn(OH)_4^{2-} + 4H_2O \tag{2}$$

$$3Zn^{2+} + 2PO_4^{3-} \xrightarrow{\text{)))}} Zn_3(PO_4)_2 \tag{3}$$

$$3Zn(OH)_4^{2-} + 2PO_4^{3-} \xrightarrow{\text{)))}} Zn_3(PO_4)_2 + 12OH^- \tag{4}$$

where the symbol))) denotes ultrasonic irradiation.

Figure 2 shows the XRD pattern of zinc phosphate nanospheres shown in Figure 1(a). Since there was no diffraction peaks observed from crystalline structures or other impurities, it is noted that pure amorphous zinc phosphate nanospheres were synthesized under the current sonochemical approach. This is consistent with the results of the TEM and electron diffraction pattern analyses as shown in the inset of Figure 2. The TEM (left inset in Figure 2) and the electron diffraction pattern (right inset in Figure 2) give the evidence again that as-prepared zinc phosphate nanospheres are noncrystalline. Because of their noncrystalline characteristic, quantitative and qualitative analyses were additionally conducted by EDX and FT-IR spectroscopies, respectively, in order to investigate the chemical composition of as-prepared zinc phosphate nanospheres.

EDX analysis confirmed that as-prepared nanospheres were composed of Zn, P, and O components only. The atomic ratio

Figure 1. SEM images of amorphous zinc phosphate nanospheres synthesized at (a) 15 mL ammonia/85 mL DI (2.36 M ammonia), (b) 20 mL ammonia/80 mL DI (3.14 M ammonia), and (c) 30 mL ammonia/70 mL DI (4.71 M ammonia) aqueous solutions. The concentration level of zinc phosphate, an intensity of ultrasonic wave, and reaction time were fixed at 0.01 M, 39.5 W/cm^2, and 30 min, respectively. (d) Changes in diameter of amorphous zinc phosphate nanospheres as a function of the volume of ammonia water used in precursor solutions. Closed circles represent average diameters, and standard deviation is shown as error bars.

Figure 2. A XRD graph of the zinc phosphate nanospheres synthesized at 2.36 M ammonia aqueous solution. Left and right insets are a TEM image and electron diffraction pattern of an individual nanosphere, respectively.
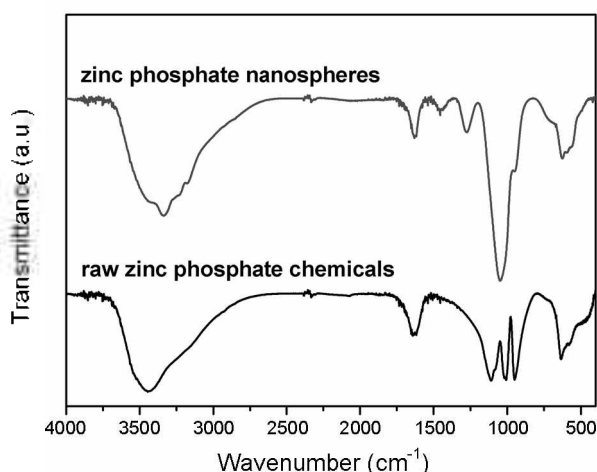
Figure 3. FT-IR spectra of amorphous zinc phosphate nanospheres (upper line) and raw zinc phosphate tetrahydrate chemicals (lower line).

of Zn/P was about 3/2, which corresponds with the $Zn_3(PO_4)_2$. The upper line in Figure 3 shows the FT-IR spectrum of as-prepared nanospheres. In order to verify that our as-synthesized nanospheres were zinc phosphate, the FT-IR analysis was also conducted using typical zinc phosphate chemicals (zinc phosphate tetrahydrate) as a reference (lower line in Figure 3). The broad bands centered at 3347 cm^{-1} (ref: 3443 cm^{-1}) is ascribed to the O-H stretching vibration. In addition, the strong vibrational band at 1632 cm^{-1} was attributed to H_2O bonding. It is noted that as-prepared zinc phosphate nanospheres are forms of hydrate.

The FT-IR spectra shows characteristic bands related to PO_4^{3-} and H_2O. The broad bands shown at 400 ~ 700 cm^{-1} (peak at 630 cm^{-1}) and 900 ~ 1300 cm^{-1} (ref: 900 ~ 1200 cm^{-1}) were attributed to the bending and complex stretching vibrations of PO_4^{3-} group, respectively.[24] In the reference FT-IR spectrum, the vibrational bands split into three distinct peaks: 954 cm^{-1}, 1021 cm^{-1}, 1107 cm^{-1} due to P-O bending, antisymmetric stretching of PO_4^{3-}, and symmetric stretching of PO_4^{3-}, respectively.[10] The significant differences between the reference FT-IR spectrum and the FT-IR spectrum of as-prepared nanospheres are the chemical shift of peaks, relative peak intensity, and the overlap between peaks in the vibrational bands. In our zinc phosphate nanosphere system, a very strong peak at 1050 cm^{-1} was observed due to the antisymmetric stretching of PO_4^{3-} with a shoulder peak at 945 cm^{-1} originated from P-O bending. A small peak at 1270 cm^{-1} originated from symmetric stretching of PO_4^{3-} was red-shifted from the reference peak. We believe that these significant differences were observed due to the crystallographic difference between our noncrystalline zinc phosphate nanospheres and typical crystalline zinc phosphate chemicals.

Conclusions

We demonstrated a simple sonochemical route to the selective synthesis of amorphous zinc phosphate nanospheres under ambient conditions. The average diameter of amorphous nanospheres could be controlled from 210 nm to 1000 nm. Ammonia concentration level in aqueous precursor solution was an important factor in the diameter control of zinc phosphate nanospheres. Based on fast, simple, convenient, economical, and environmentally benign characteristics, we expect that this sonochemical technique can be very useful in seeking to design zinc phosphate nanostructures with various morphologies.

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