

Supporting Information

Sonochemical preparation of zinc phosphate hexagonal bipyramids

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1. TEM-EDX characterization of zinc phosphate hexagonal bipyramids.

The chemical composition of hexagonal bipyramids was investigated by TEM-EDX spectroscopy. In Figure S1, EDX confirmed that as-prepared hexagonal bipyramids were composed of Zn, O, and P components only. Carbon (C) and copper (Cu) components were originated from the Cu TEM grid covered with carbon support film (Ted Pella, Inc. Prod No. 01881-F).

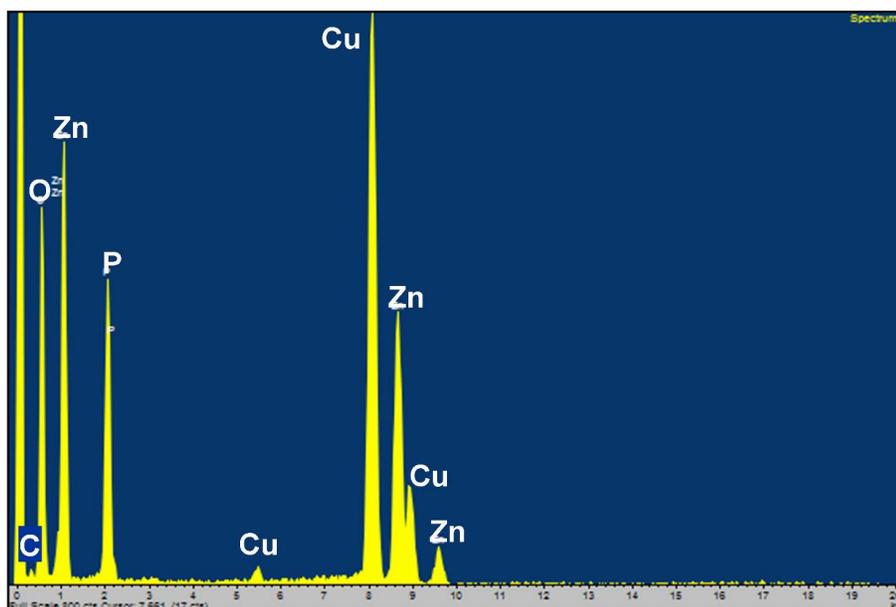


Figure S1. A TEM-EDX spectrum of as-prepared zinc phosphate hexagonal bipyramids.

2. Reference FT-IR spectrum of zinc phosphate.

In order to acquire reference spectrum of zinc phosphate, the FT-IR analysis was conducted using commercial zinc phosphate chemicals (zinc phosphate tetrahydrate, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, 98%, Junsei). The FT-IR spectrum shows characteristic bands related to PO_4^{3-} and H_2O . The broad bands shown at $400\sim 700\text{ cm}^{-1}$ (peak at 627 cm^{-1}) and $900\sim 1200\text{ cm}^{-1}$ were attributed to the bending and complex stretching vibrations of PO_4^{3-} group, respectively (O. Pawlig *et al.*, *Mater. Res. Bull.* 1999, **34**, 1959). In detail, the vibrational bands from $900\sim 1200\text{ cm}^{-1}$ split into three distinct peaks: 954 , 1021 , and 1107 cm^{-1} due to P-O bending, antisymmetric stretching of PO_4^{3-} , and symmetric stretching of PO_4^{3-} , respectively (A. Q. Yuan *et al.*, *Mater. Lett.* 2006, **60**, 2110). The strong vibrational band at 1626 cm^{-1} was attributed to H_2O bonding. In addition, the broad bands centered at 3443 cm^{-1} is ascribed to the O-H stretching vibration.

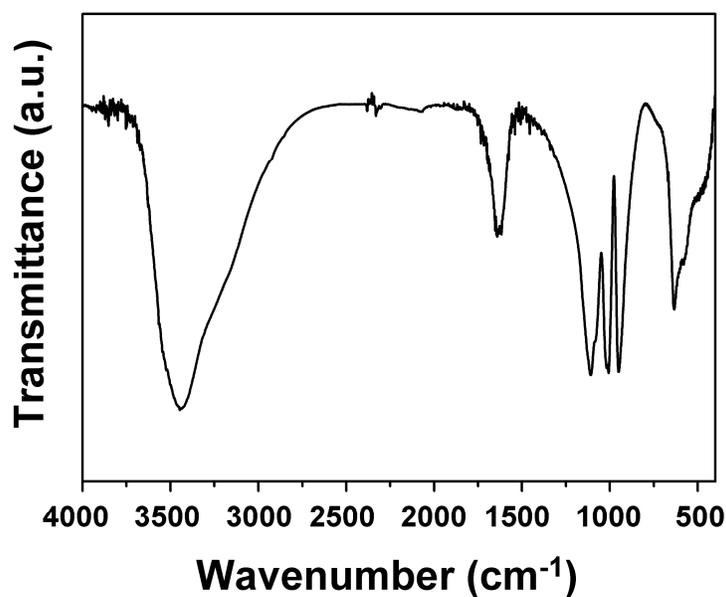


Figure S2. A FT-IR spectrum of commercial zinc phosphate tetrahydrate, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

3. XRD analyses of as-prepared zinc phosphate crystals synthesized with or without ultrasonication.

In order to compare the phase of as-prepared zinc phosphate crystals synthesized with or without ultrasonication, the XRD analyses were conducted using zinc phosphate crystals synthesized by (i) vigorous stirring for 20 min without ultrasonication and additional heating, (ii) vigorous stirring for 3 hrs at 80 °C which is the steady temperature in our ultrasonic reaction, and (iii) ultrasonication for 20 min at an intensity of 39.5 W/cm². Figure S3 shows the XRD patterns of as-prepared zinc phosphate crystals. As shown in Figure S3, three kinds of as-prepared zinc phosphate crystals have similar XRD patterns, except for relative peak intensity levels which were due to the random orientation. The XRD analyses confirmed that as-prepared zinc phosphate crystals synthesized with or without ultrasonication belonged to the same phase. This was because there was no diffraction peaks observed from other impurities in the XRD patterns.

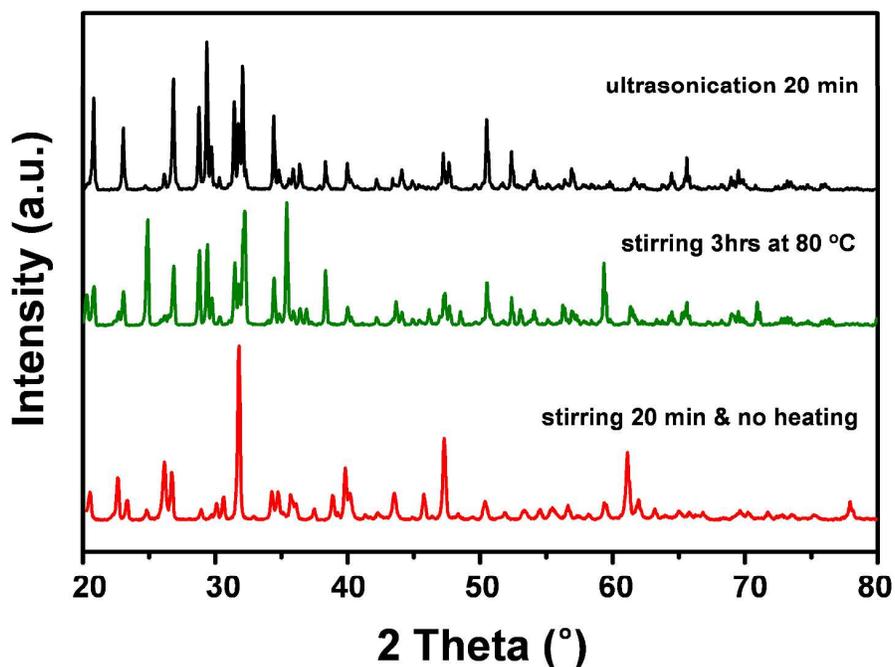


Figure S3. The XRD patterns of as-prepared zinc phosphate crystals synthesized with of without ultrasonication.

4. SEM analysis of zinc phosphate crystals synthesized under different reaction times.

A series of experiments was conducted to investigate the effect of reaction time on the formation of zinc phosphate hexagonal bipyramids. A mixture of 0.08 M sodium phosphate dibasic anhydrous aqueous solution (50 ml) and 0.02 M zinc nitrate hexahydrate aqueous solution (50 ml) was prepared at room temperature. Total concentrations of sodium phosphate dibasic anhydrous and zinc nitrate hexahydrate in the precursor solution were 0.04 and 0.01 M, respectively. After sufficient mixing, an ultrasonic wave was introduced at an intensity of 39.5 W/cm^2 for 3, 7, 10, and 15 min, respectively.

Figure S4 shows the SEM images of as-prepared zinc phosphate crystals produced under different reaction times. As shown in Figure S4a and b, when the precursor solution was ultrasonicated for 3 min, mixed powders of perfect and non-perfect hexagonal bipyramid particles were produced. The size distribution was considerably large. Very large particles were non-perfect and partially-dissolved hexagonal bipyramids in $\{011\}$ surfaces. When the precursor solutions were ultrasonicated for more than 7 min (from 7 to 15 min), mixed powders of hexagonal bipyramid particles and small amount of non-perfect hexagonal bipyramid particles were obtained as shown in Figure S4c-h. Compared with the size distribution of zinc phosphate crystals synthesized by 3 min ultrasonication, the size distribution was relatively small. For the selective production of perfect hexagonal bipyramids, it requires 20 min as a minimum reaction time in our studies.

We expect that the growth of hexagonal bipyramids is governed by a dissolution-recrystallization growth mechanism (*Cryst. Growth Des.* **2006**, *6*, 577-582). Along with this mechanism, it is thought that the initial precipitated particles started to dissolve into the solution and grow onto large particles of zinc phosphate, and hexagonal bipyramids were produced. We found that this growth mechanism is strongly affected by concentrations of Na_2HPO_4 as shown in Figure 4.

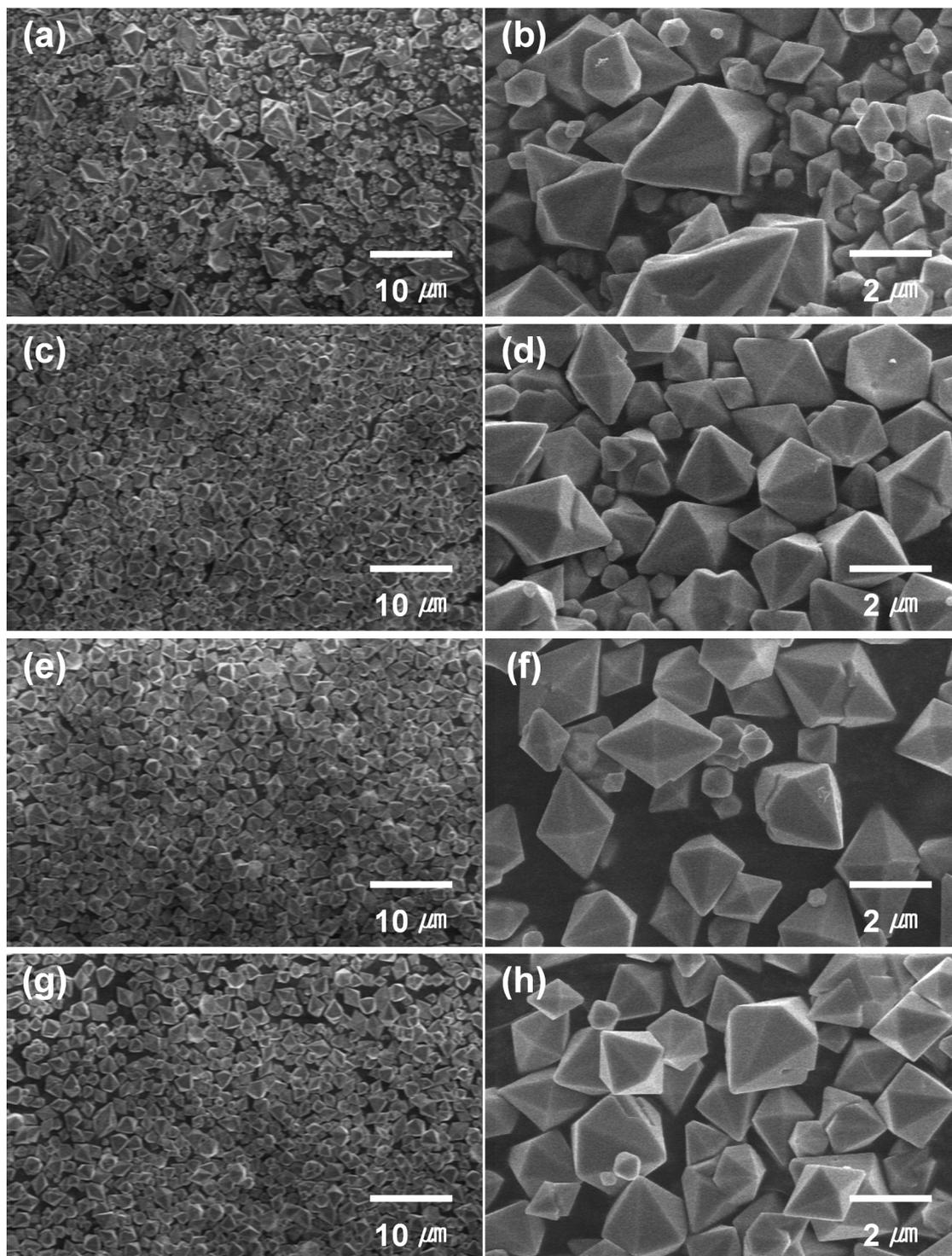


Figure S4. The low- and high-magnification SEM images of as-prepared zinc phosphate crystals synthesized under different reaction times. The reaction times were (a and b) 3, (c and d) 7, (e and f) 10, and (g and h) 15 min, respectively.