Novel Microstructures of Self-Assembled Microcrystallites of $(NH_4)_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$

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Three different microstructures of self-assembled microcrystallites (or of aggregates) of heteropoly compounds, $(NH_4)_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$, have been found: (1) microcrystallites that self-assembled with unidirectional orientation and were epitaxially connected with each other to form dodecahedra, (2) microcrystallites that self-assembled with unidirectional orientation, but were little connected epitaxially each other to form round aggregates, and (3) dispersed fine particles. This variation of the microstructure was consistently explained by the change in the solubility of the compounds, that is, the precipitation temperature and the kind of cation.

Recently, the self-assembly of particles or microcrystallites, that is, the aggregates, with dimensions of the order of 100 nm or above has attracted much attention as a strategy to design new materials.[1-4] However, the self-assembling mechanism of the microcrystallites is still a subject to be elucidated. We previously reported the formation of porous aggregates of an ammonium salt of heteropolyacid, $(NH_4)_3PW_{12}O_{40}$, in which microcrystallites were epitaxially connected each other to form a dodecahedral shape.[5]

Here we report that a variety of microstructures of self-assembled $(NH_4)_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ microcrystallites are formed by changing the counter cation and the precipitation temperature. It seems that the solubility of the compounds is essential in determining the microstructure and the shape of the aggregates.

$(NH_4)_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ were prepared as follows: Stoichiometric amount of aqueous solution of NH_4HCO_3 (0.055 mol dm^{-3}, ca. 40 cm^3) or Cs_2CO_3 (0.048 mol dm^{-3}, ca. 23 cm^3) was added dropwise to aqueous solution of $H_3PW_{12}O_{40}$ (ca. 30 cm^3, 0.025 mol dm^{-3}) with vigorous stirring in ca. 90 min to precipitate salts. The temperature of $H_3PW_{12}O_{40}$ solution during the precipitation was kept at an elevated temperature (368 K) or at a lower temperature (273 K or 298 K). White colloidal solutions formed were dried up at 328 K with a vacuum rotary evaporator to obtain white powder of the salts. Hereafter, these $(NH_4)_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ are designated by NH_4-t and Cs-t, respectively, where t indicates the precipitation temperature (for example, NH_4-368 means $(NH_4)_3PW_{12}O_{40}$ prepared at 368 K). Electron diffraction (ED) experiments were carried out to measure the crystal orientation of microcrystallites. N_2 adsorption isotherms were measured at 77 K. For each of NH_4 and Cs salts, powder X-ray diffraction (XRD) gave identical patterns regardless of the precipitation temperature except for the line widths. The diffraction patterns showed cubic structures with 11.7 and 11.9 Å of lattice constants for the NH_4 and Cs salts, respectively, in which Keggin anions, $PW_{12}O_{40}^{3-}$, are densely packed to form a bcc structure similar to $H_3PW_{12}O_{40} \cdot 6\,H_2O$.[6] Micropore does not exist in this crystal structure.

The sizes of microcrystallites were calculated from the BET surface area assuming spherical shape, and the lengths of ordered crystal structure were estimated by the Scherrer's method from the calibrated (222) linewidth of XRD as in the previous report.[5] These values are denoted here by d(BET) and L(XRD), respectively. The ratio of L(XRD) / d(BET) can be used as an index of the extent of the "epitaxial connection" between microcrystallites: If this value is much higher than unity, the ordering of Keggin anions continues to a much longer distance than the size of the microcrystallites. In other words, the microcrystallites are connected by epitaxial interfaces wide enough to make them coherent with respect to X-ray diffraction. If the microcrystallites are randomly oriented and little connected with each other, the ratio becomes close to unity.

Figure 1a and b shows SEM images of NH_4-273 and Cs-368. Before we discuss the unique microstructure of these two samples, typical microstructures shown in Figure 1c and d will be explained. In Figure 1c is shown the SEM image of NH_4-368 which formed symmetric dodecahedral aggregates by epitaxial self-assembly of microcrystallites.[5] For this sample, as reported previously,[5] the L(XRD) and d(BET) were 81-150 nm (L(XRD) was variable to some extent upon water adsorption) and 16 nm, respectively, giving much larger L(XRD) / d(BET) ratios than unity. Therefore, the microcrystallites were connected epitaxially in an aggregate, and the regular spots of ED observed for this sample support the unidirectional crystal orientation of the microcrystallites. Hence

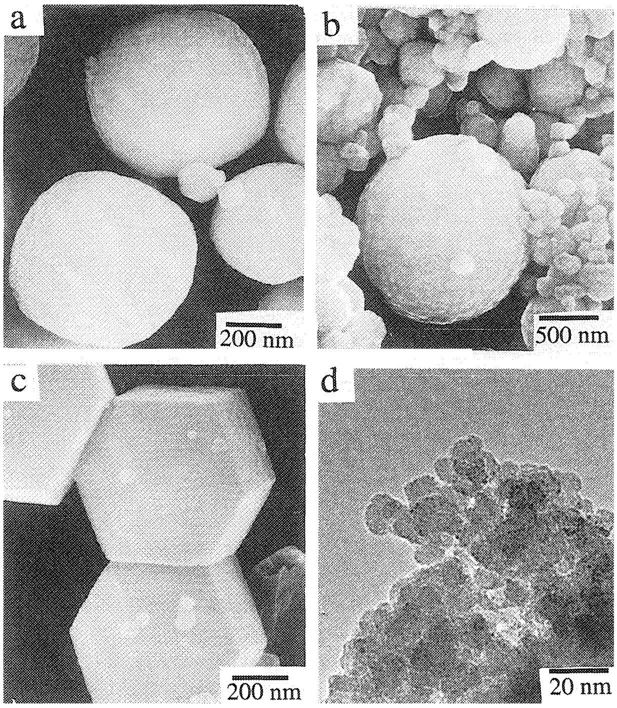

Figure 1. SEM images of (a) NH_4-273, (b) Cs-368, and (c) NH_4-368, and (d) TEM image of Cs-298. See text.

this aggregate looks like a porous single crystal. The variation of the rate of titration in from 1 to 180 min little influenced the structure of NH_4-368. Figure 1d shows the transmission electron microscope (TEM) image of Cs-298 (precipitated at a low temperature). Well-dispersed particles with diameters of ca. 10 - 15 nm were observed. ED of this sample gave a ring pattern, demonstrating that the crystal orientation of the microcrystallites was random. L(XRD) are comparable with d(BET).[5] Hence, this case is the ordinary random aggregates of microcrystallites.

On the other hand, round aggregates are observed for the two samples in Figure 1a and b, while the sizes of the aggregates of the latter showed a rather wide distribution. Their high BET surface areas (117 and 85 $m^2 g^{-1}$ for NH_4-273 and Cs-368, respectively) demonstrate that these aggregates are also highly porous. The outer surface areas estimated by the SEM images are 2 to 5 $m^2 g^{-1}$. The L(XRD) for NH_4-273 and Cs-368 are 25 and 24 nm, respectively. These values are comparable with their d(BET), 8 and 12 nm, giving a low L(XRD) / d(BET) ratio of ca. 3 and 2 for NH_4-273 and Cs-368, respectively. These low values indicate that the epitaxial connections were little formed, in contrast to the dodecahedra of NH_4-368 (Figure 1c).

Figure 2 shows ED of the round aggregate of Cs-368 shown in Figure 1b. Although the diffraction of the entire round aggregate was taken (Figure 2b), regular discrete spots were observed (Figure 2a), which are rationally interpreted by assuming electron incident in the [111] direction. This demonstrate that the microcrystallites in the aggregate have the same crystal orientation even for the round aggregates having low L(XRD) / d(BET) ratios. Similar results were obtained also for the round aggregates of NH_4-273 shown in Figure 1a. This type of microstructure is unique, as ED shows a unidirectionally oriented aggregate, but XRD indicates that it is polycrystalline. The origin of the orientation is not clear at present. A possible mechanism, for example, is that the microcrystallites have regular shapes and are stacked with such orientation, or that small but strong epitaxial contacts between microcrystallites control the orientation.

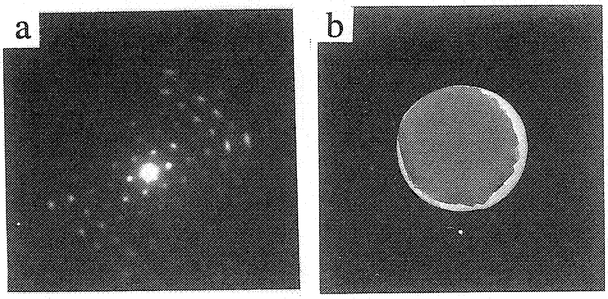

Figure 2. (a) Electron diffraction of Cs-368. (b) The area in which (a) was taken.

Figure 3 shows an AFM image of the surface of NH_4-273. It can be seen that the microcrystallites of ca. 6 nm in diameter array themselves in a somehow regular way, although the packing of microcrystallites is not a simple closest packing such as bcc or hcp. This is the first direct observation by AFM of the self-assembled microcrystallites of heteropoly compounds. The size of microcrystallites seen by AFM, ca. 6 nm, is close to d(BET), 8 nm, suggesting that the aggregates of NH_4-273 entirely consist of microcrystallites of this size. A similar AFM image was obtained for NH_4-368, indicating that the size of microcrystallites was also ca. 6 nm.

As described above, there were three different microstructures; (1) microcrystallites that self-assembled with unidirectional orientation and were epitaxially connected with each other to form dodecahedra (NH_4-368, Figure 1c),[5] (2) microcrystallites that self-assembled with unidirectional orientation but little connected epitaxially to form round aggregates (NH_4-273, Cs-368, Figure 1a and b), and (3) dispersed fine particles (Cs-273, Figure 1d). Among them, the microstructure of the second case is novel. The other two were reported previously.[5] The results demonstrate that the precipitation temperature and counter cations are very influential on the microstructure of the aggregate. As the temperature decreases, the structure changes from (1) to (2) for NH_4 salts and from (2) to (3) for Cs salts. In addition, at the same temperature, the NH_4 salt tends to be more nearly epitaxial than the Cs salt. Considering the higher solubility of $(NH_4)_3PW_{12}O_{40}$ than $Cs_3PW_{12}O_{40}$, even though their solubilities are both very low, and the aforementioned temperature dependency, the solubility of the salts at the precipitation temperature seems to control the microstructure. The higher the solubility is, the more the epitaxial connection was formed, that is, the variation from (3) (Figure 1d) through (2) (Figure 1a and b) to (1) (Figure 1c) takes place.

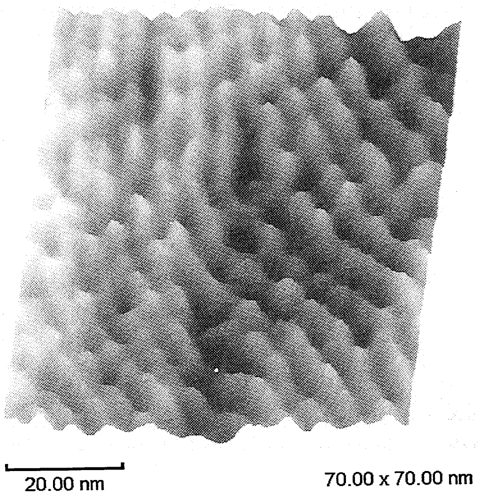

Figure 3. AFM image of NH_4-273.

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References and Notes

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