# Monodispersed Microporous Polyoxotungstate with Regular Shape

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Monodispersed fine particles of $(NH_4)_3PW_{12}O_{40}$ having regular shape were successfully prepared as precipitates by the titration of $NH_4HCO_3$ solution to $H_3PW_{12}O_{40}$ solution. The particles were ca. 1 µm in size and microporous with 151 $m^2$ $g^{-1}$ of BET surface area. AFM image demonstrated that these particles were aggregates of nanocrystallites of ca. 15 nm in size.

Monodispersed colloidal particles are promising materials for electronics devices, recording materials, pigments and catalysts,[1] and at the same time interesting subjects of theoretical research.[2] Under certain conditions, they self-assemble into a three-dimensional lattice known as colloidal crystals.[3] In order to prepare such monodispersed particles, a method using reverse micells[4] or precipitation from homogeneous solutions[5] has been devised. Simple methods such as titration method have scarcely been employed.[6] In the case of microporous particles of µm-order, an elaborate method is usually required.[7] Here we report a very simple method for the preparation of µm-order monodispersed particles of polyoxotungstate, $(NH_4)_3PW_{12}O_{40}$, which were precipitated by titration of $NH_4HCO_3$ solution to an aqueous solution of $H_3PW_{12}O_{40}$. They had microporosity as well as high surface area.

$H_3PW_{12}O_{40}\cdot 6H_2O$ was first prepared by evacuation at 323 K. Then, stoichiometric amount of aqueous solution of $NH_4HCO_3$ (typically 0.45 mmol, 3 mL of 0.15 M solution) was added dropwise using a Pasteur pipette to aqueous solution of $H_3PW_{12}O_{40}\cdot 6H_2O$ (typically 0.15 mmol, 60 mL of 0.0025 M solution) with vigorous stirring. Typically, 0.25 mL of $NH_4HCO_3$ solution (ten drops) was added 12 times at 1 min interval to obtain monodispersed particles. These are designated as **A**. The concentrations of $NH_4HCO_3$ (0.0075–0.75 M) and $H_3PW_{12}O_{40}$ (0.0025–0.25 M) solutions as well as the rate of the addition of $NH_4HCO_3$ solution were changed in some cases. The other samples denoted by **B** were prepared by the previous method[8] in which aqueous solution of $NH_4HCO_3$ (0.055 M) was added dropwise to aqueous solution of $H_3PW_{12}O_{40}\cdot 6H_2O$ (0.025 M) with the rate of 0.40 mL $min^{-1}$. In each case, the temperature of $H_3PW_{12}O_{40}$ solution was kept at 368 K during the titration. After aged for 30 min at 368 K and cooled to room temperature, white suspensions resulted and they were dried up at 328 K with a vacuum rotary evaporator to obtain white powder of $(NH_4)_3PW_{12}O_{40}$. The yield of the powder was above 80%. The samples were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Nitrogen adsorption isotherms were measured at 77 K. Powder X-ray diffraction patterns showed cubic structure with 1.17 nm of lattice constant. The average sizes of the nanocrystallites were calculated from the BET surface areas assuming spherical shape. The lengths of ordered crystal structure were estimated by the Scherrer equation from the (222) linewidth of XRD as in the previous study.[8] These values are denoted by *d*(BET) and *L*(XRD), respectively.

Figure 1a shows SEM image of particles of **A**, which indicates sharp size distribution. They were dodecahedra with slightly round edges, and all particles observed were ca. 1 µm in size. When a drop of *n*-hexane in which **A** was dispersed was deposited on a slide glass and allowed to dryness in air, the particles self-assembled into two-dimensional closely packed colloidal array as shown in Figure 1b. This demonstrates that the size of these particles was uniform and the shape was regular. In this respect, these particles may be regarded monodispersed (note that **B** did not show sharp size distribution (0.3 – 1 µm)[8]).

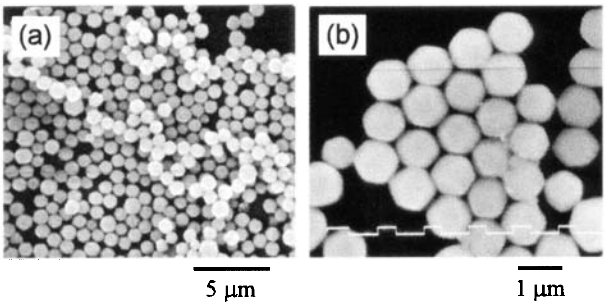

**Figure 1.** SEM images of monodispersed $(NH_4)_3PW_{12}O_{40}$. (a) lower magnification, and (b) higher magnification.

The monodispersed particles were formed more readily when the concentration of $H_3PW_{12}O_{40}$ solution was low. There are proper combinations of the rate of titration and the concentration of $NH_4HCO_3$ in order to prepare monodispersed particles like those shown in Figure 1. The size of monodispersed particles decreased when the rate of titration was low (one drop of $NH_4HCO_3$ solution was added at 1 min interval). The particles were not monodispersed when the concentration of $NH_4HCO_3$ was 0.375 M (2.5 × standard concentration (= 0.15 M)).

Figure 2a shows the $N_2$ adsorption isotherm of **A**. The isotherm of **B** is given for comparison (Figure 2b). Both isotherms were of Type I, typical of microporous materials.[9] The larger initial uptake observed for the isotherm of **A** indicates that it has more micropores than **B**. Actually, total pore volume of **A**, 0.075 $cm^3$ $g^{-1}$, was twice as large as that of **B**, 0.036 $cm^3$ $g^{-1}$. Besides, **A** had a quite large BET surface area of 151 $m^2$ $g^{-1}$ compared with **B** (65 $m^2$ $g^{-1}$). It is worthy to comment that colloidal particles of µm-order rarely have microporosity or high surface area.[7,10]

**A** was characterized also by AFM. Figure 3 shows the surface image. Nanocrystallites of ca. 15 nm in size were observed on the surface, which are considered to be the primary particles. Similar images of nanocrystallites were obtained by SEM, as well. Therefore, **A** is aggregates of fine nanocrystal-

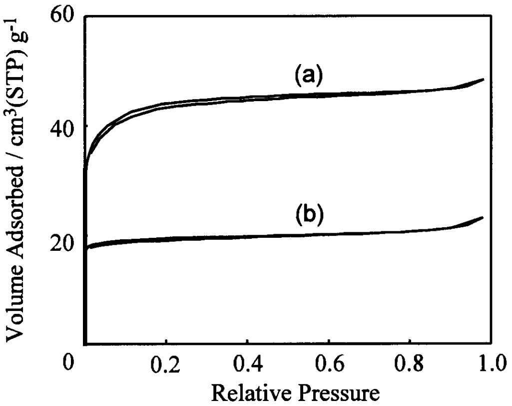

**Figure 2.** $N_2$ adsorption isotherms of $(NH_4)_3PW_{12}O_{40}$. (a) monodispersed (**A**), and (b) previously prepared (**B**).[8]

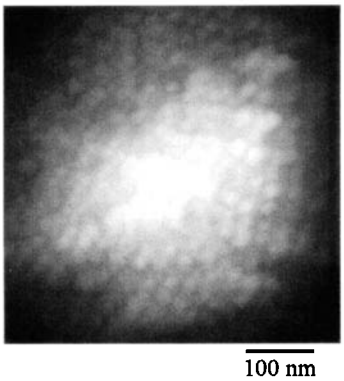

**Figure 3.** AFM image of the surface of monodispersed $(NH_4)_3PW_{12}O_{40}$.

lites like in the case of **B**.[8]

*d*(BET) and *L*(XRD) of **A** were 7 nm and 2.0 × 10$^2$ nm, respectively, which lead to *L*(XRD)/*d*(BET) of ca. 30. Since the *L*(XRD)/*d*(BET) of **B** was 5.3 – 9.9,[8] the crystallinity of **A** is much greater than **B**. Although electron diffraction was not measured for **A**, the higher value of *L*(XRD)/*d*(BET) demonstrates that **A** is also epitaxial aggregates as in the case of **B**.

The major differences in the preparation procedure between **A** and **B** were the concentrations of $H_3PW_{12}O_{40}$ and $NH_4HCO_3$; the former was lower and the latter higher for **A**. The low concentration of $H_3PW_{12}O_{40}$ probably provides uniform reaction field, so that nanocrystallites with uniform and smaller size is favored and aggregates formed have uniform and regular inner structure. In turn, smaller nanocrystallites give a larger BET surface area.

In summary, monodispersed ammonium salt of $H_3PW_{12}O_{40}$ was prepared by simple titration in aqueous media. The particles were microporous and ca. 1 μm in size, having high surface area and regular shape. These porous particles form regular self-assembled two-dimensional array (Figure 1b). This microporous colloidal array would be utilized to develop novel functional materials taking advantage of their regular hierarchical structure composed of nanocrystallite, monodispersed aggregate, and regular colloidal array.

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## References and Notes

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10 Zeolite particles of μm-order, which include single crystals of many types of zeolite, have microporosity.