

## Hierarchical design of nanostructured materials based on polyoxometalates\*

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*Abstract:* The construction of nanostructured materials with advanced functions by the self-organization of molecular building blocks is one of the key topics in modern materials chemistry. This review describes our concept of the hierarchical design of polyoxometalate (POM)-based compounds with nanosized spaces: (1) syntheses of building blocks (POMs and counter cations), (2) directing the self-organization of building blocks to form crystalline materials with nanosized spaces, and (3) kinetic control of the self-organization process to introduce nanosized space into the dense nonporous crystal, with emphasis on (2). Our recent results on the construction of nanosized spaces within the POM-based compounds with controlled size, volume, shape, and affinity, and their functions are presented.

*Keywords:* encapsulation; nanosized space; nanostructured materials; polyoxometalate; sorption.

### INTRODUCTION

The arrangement of molecular building blocks into ordered structures by the bottom-up approach is one of the key topics in modern materials chemistry. Precise control of the arrangements at the atomic/molecular level would allow the development of nanostructured materials exhibiting predesigned functionality. The design of such systems requires the use of molecular building blocks with well-defined size, shape, elemental composition, and electronic configuration. Especially, the design and synthesis of materials with nanosized space have attracted the attention of chemists because of their interest in the unique guest sorption, exchange, or isolation properties [1–7]. These materials as hosts can be classified into two groups: materials with infinite structures [1–4] and discrete structures (supramolecules) [5–7]. Classical examples of host materials with infinite structures are zeolites which are composed of covalently bonded  $[\text{TO}_4]$  units ( $T = \text{Si}, \text{Al}$ ). The pore entrance of Na–A zeolite is built with eight covalently bonded  $[\text{TO}_4]$  units, and  $\text{Na}^+$  resides in the pore [8]. The effective pore diameter is 3 Å, and ethane can enter the pore, while larger *n*-butane is excluded [8]. The exchange of  $\text{Na}^+$  with  $\text{Ca}^{2+}$  increases the effective pore diameter from 3 to 5 Å since  $\text{Ca}^{2+}$  cannot reside in the pore because of the larger ionic radius, and Ca–A zeolite can sorb *n*-butane [8]. Recently, metal–organic frameworks, which are constructed with the coordination bonds between the metal ions and organic units, have received much attention because the framework geometries can be finely tuned by the choice of building blocks [3,4]. Examples of host materials with discrete structures (supramolecules) can be seen in nature for the highly specific, selective, and cooperative biological systems such as valinomycin for the  $\text{K}^+$  transport

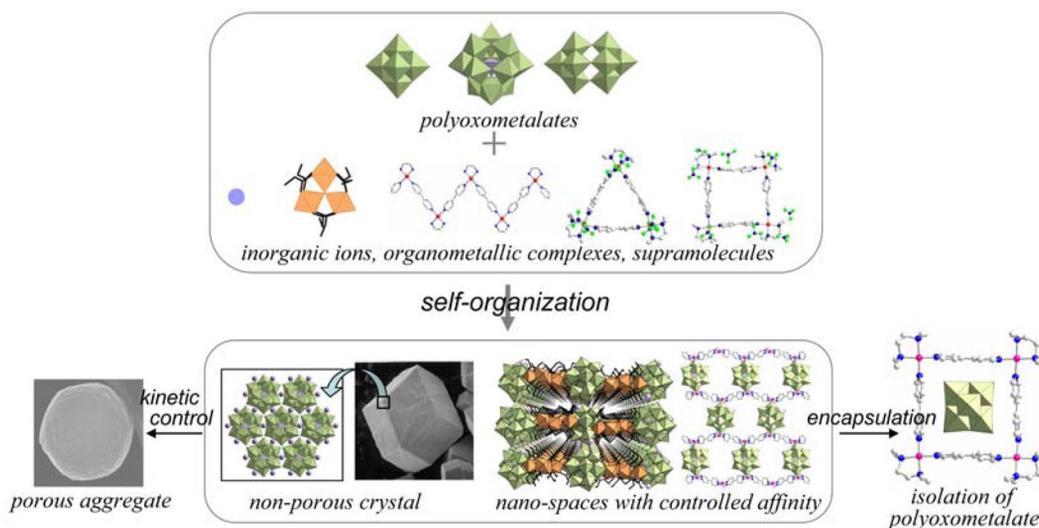
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[9]. Classical examples of synthetic supramolecules are crown ethers and cryptands, which are cyclic organic molecules and exhibit the size-selective binding of cations [10]. Cyclodextrins and calixarenes incorporate both neutral and cationic guests into their cavities [10]. Recently, metal ions have been widely used to synthesize supramolecules because the metal ions possess diverse functions as well as coordination geometries directing the syntheses of supramolecules. For example, *cis*-protected square planar metal cations [Pd(II) and Pt(II)] and organic bridging ligands are found to self-organize into molecular polygons [5,6].

Polyoxometalates (POMs) are nanosized anionic metal-oxygen clusters of early transition metals and have stimulated research in broad fields of science such as catalysis, electrochemistry, magnetism, and medicine [11–13]. The chemical properties of POMs or POM-based compounds such as the redox potential, acidity, and solubility can be finely tuned by the choice of the size, shape, composition, electronic configuration, or counter cation [11–13]. The self-organization of POMs with appropriate counter cations can form nanostructured compounds with predesigned functionality [14–19]. Due to the strong and isotropic ionic bonds, these anions and cations are often closely packed in the crystal lattice. For example, Keggin-type phosphotungstate  $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$  and  $\text{NH}_4^+$  form an all-inorganic single crystal of  $(\text{NH}_4)_3[\alpha\text{-PW}_{12}\text{O}_{40}]$  in an aqueous solution at 473 K [20]. The single-crystal X-ray structure analysis shows that  $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$  and  $\text{NH}_4^+$  are closely packed in a cubic lattice and that no intrinsic pores exist [20].

There are several ways to introduce well-defined nanospaces into the POM-based materials. The use of cationic organometallic complexes or supramolecules directs the self-organization of the building blocks into regulated structures according to the size, shape, charge, and functional group of the cations to construct materials with controlled pore size, pore volume, and hydrophilicity/-phobicity [21–24]. The kinetic control of the self-organization process by the changes in the synthetic conditions can form porous aggregates instead of nonporous single crystals [25]. These ideas are schematically shown in Fig. 1. In the following sections, the concept of the hierarchical design of the nanostructured materials and their chemical properties according to these ideas are described.



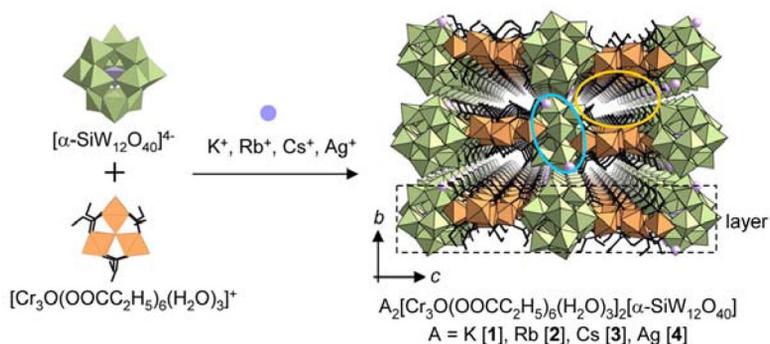
**Fig. 1** Hierarchical design of nanostructured materials by the self-organization of POMs and counter cations (inorganic ions, organometallic complexes, and supramolecules).

## FLEXIBLE NANOSPACES WITH CONTROLLED AFFINITY

### Use of organometallic complexes as counter cations of POMs

The partial exchange of the alkali metal cations of a Keggin-type silicotungstate with the cationic organometallic complex  $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^+$  formed porous compounds with the formula of  $\text{A}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  ( $\text{A} = \text{K}$  [1],  $\text{Rb}$  [2],  $\text{Cs}$  [3]) [21]. These compounds were composed of 2D layers of  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^+$ . In the layers parallel to the *ac*-plane,  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^+$  were arranged in honeycomb patterns by the hydrogen bonds and ionic bonds. The layers were stacked along the *b*-axis with an offset of  $a/2$  with respect to each other, and alkali metal ions resided between the adjacent layers. Compounds **1–3** possessed hydrophobic channels surrounded by the propionate ligands of  $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^+$  and hydrophilic channels comprising hydrogen-bonded networks of the water of crystallization. The increase in the size of the alkali metal ion from  $\text{K}^+$  ( $r = 1.52 \text{ \AA}$ ) to  $\text{Rb}^+$  ( $r = 1.66 \text{ \AA}$ ) or  $\text{Cs}^+$  ( $r = 1.81 \text{ \AA}$ ) increased the interlayer spacing, and the size of the opening of the hydrophobic channel increased in the order of **1** ( $2.5 \times 5.1 \text{ \AA}$ ) < **2** ( $3.4 \times 5.1 \text{ \AA}$ ) < **3** ( $4.0 \times 5.2 \text{ \AA}$ ). In particular, **3** sorbed water and dichloromethane into the hydrophilic/-phobic channel, respectively, and realized the adsorptive separation of a gas mixture of water and dichloromethane [26].

In order to further functionalize these compounds, we focused on the adsorptive separation of olefin/paraffin, which represents an industrially important and scientifically interesting separation process [27]. It has been recognized that the utilization of the  $\pi$ -complexation between the  $\pi^*$  orbital of  $\text{C}=\text{C}$  ( $\text{C}\equiv\text{C}$ ) and the *d* orbital of the metal cation with  $d^{10}$ -electronic configuration (e.g.,  $\text{Ag}^+$ ) is promising for the selective sorption of olefins [28]. Based on these considerations,  $\text{Ag}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  [**4**] was synthesized by the exchange of alkali metal ions with  $\text{Ag}^+$  [22]. While **4** was isostructural with **1–3**, the interlayer spacing was small and no channels existed because of the smaller size of  $\text{Ag}^+$  ( $r = 1.29 \text{ \AA}$ ) compared with the alkali metal ions ( $r = 1.52\text{--}1.81 \text{ \AA}$ ) (Fig. 2).



**Fig. 2** Syntheses and crystal structures of **1–4** along the *a*-axis. Orange and blue ovals show the hydrophobic/-philic channel, respectively.

The sorption isotherms of **4** at 298 K showed that the amounts of sorption of small unsaturated hydrocarbons such as ethylene, propylene, *n*-butene, acetylene, and methyl acetylene were  $>1 \text{ mol mol}^{-1}$ , while those for paraffins and larger unsaturated hydrocarbons were smaller than the amounts of sorption on the external surface ( $<0.2 \text{ mol mol}^{-1}$ ). Especially, fine crystals of **4** exhibited ethylene/ethane and propylene/propane sorption ratios over 100 at 298 K and 1 atm, and the values were larger by 1 order of magnitude than those reported [29]. The sorption property could be applied to the collection of ethylene from the gas mixture of ethane and ethylene. The kinetic analysis of the sorption

profile of ethylene showed that ethylene molecules in the gas phase were adsorbed on the external surface and subsequently diffused into the solid bulk. In situ powder X-ray diffraction (XRD) studies showed that the lattice volume of **4** increased by  $766 \text{ \AA}^3$  per unit cell with the sorption of  $2 \text{ mol mol}^{-1}$  of ethylene ( $655 \text{ \AA}^3$ ), showing a flexible framework of **4**. In situ IR studies showed that the  $\nu(\text{C}\equiv\text{C})$  band of gaseous methyl acetylene shifted to the lower wavenumber by ca.  $100 \text{ cm}^{-1}$ , suggesting the  $\pi$ -complexation between  $\text{Ag}^+$  and methyl acetylene [30]. These results show that paraffins can only be sorbed on the external surface while small unsaturated hydrocarbons can penetrate into the solid bulk with an increase in the lattice volume through the  $\pi$ -complexation with  $\text{Ag}^+$ , resulting in the high olefin/paraffin (ethylene/ethane and propylene/propane) sorption ratios (Fig. 3).

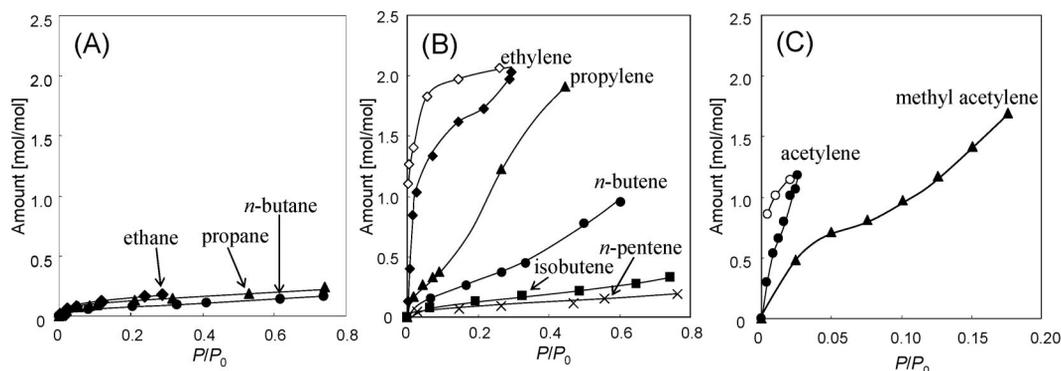


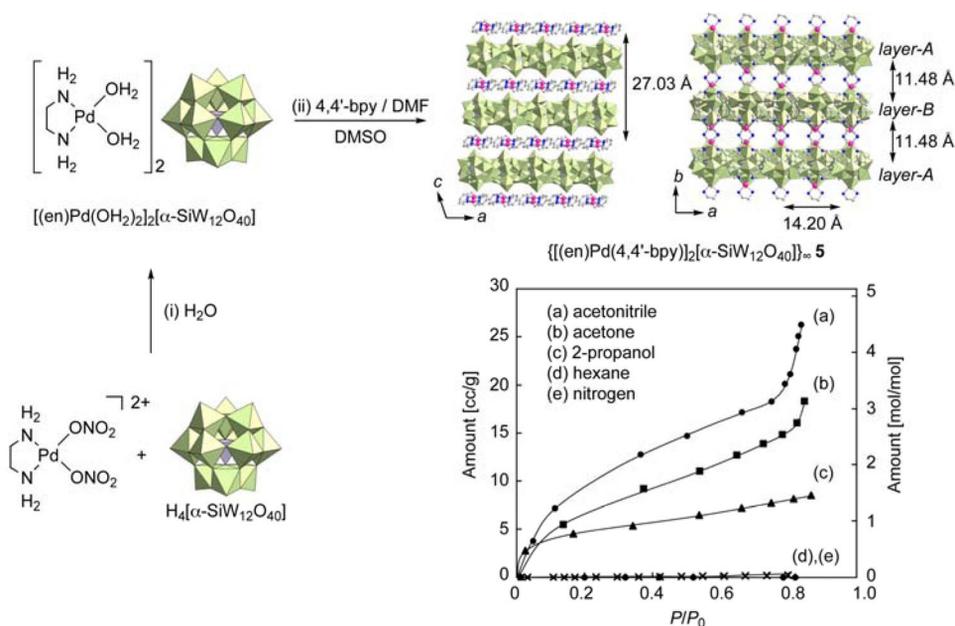
Fig. 3 Sorption isotherms of **4** at 298 K. (a) Paraffins, (b) olefins, and (c) acetylenes.

### Use of supramolecules as counter cations of POMs

In order to further fabricate the frameworks of the POM-based compounds, supramolecules were introduced into the crystal lattice [23]. This idea would furnish the frameworks with nanosized spaces with finely controlled size, volume, and affinity, since the supramolecules are known to be synthesized by the rationally controlled self-organization process. In particular, the molecular polygons based on the *cis*-protected square planar metal cations [Pd(II) and Pt(II)] and organic bridging ligands have been extensively developed by Fujita et al. and Stang et al. [5,6]. Their strategy helped us to design the regulated frameworks inside the crystal lattice of POM-based compounds.

The starting material of the hybrid compound was synthesized by the treatment of ethylenediamine Pd complex (en)Pd(NO<sub>3</sub>)<sub>2</sub> with H<sub>4</sub>[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] in H<sub>2</sub>O (Fig. 4, path i). The resultant product was characterized as [(en)Pd(OH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>], which possessed labile water ligands at the *cis*-position of the Pd metal center, so that the product could be utilized as the building blocks of the framework structure. Successively, the reaction of [(en)Pd(OH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] with the organic bridging ligand of 4,4'-bipyridine (4,4'-bpy) was carried out (Fig. 4, path ii).

Compound **5** was an unexpected infinite chain Pd complex  $\{[(\text{en})\text{Pd}(4,4'\text{-bpy})]_2[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot 4.5\text{DMSO} \cdot 3.5\text{DMF}\}_\infty$ . The combination of the ethylenediamine Pd complex cation and the bulky Keggin-type silicotungstate prior to the addition of 4,4'-bipyridine furnished the infinite chain structure. The formation of putative molecular triangle and square is probably prevented by the steric repulsion between the infinite chain Pd complex fragment and POM [5]. The solvents of crystallization interacted with the ethylenediamine ligand by the hydrogen bonds or coordinated to the Pd metal center, and resided between the layers or inside the cavity constructed by the infinite chain Pd complex and POM. The Keggin-type POM [ $\alpha\text{-SiW}_{12}\text{O}_{40}$ ]<sup>4-</sup> connected the cationic [(en)Pd(4,4'-bpy)]<sup>2+</sup> chain to form 2D-grid layers spreading in the *ac* planes of the crystal lattice in **5**. The *layer-A* and *layer-B* were stacked alternately along the *b*-axis in the *ABAB*... fashion. The distance between the layers was calcu-



**Fig. 4** Synthesis and sorption properties of the Pd complex–POM hybrid compound with the infinite chain frameworks,  $\{[(en)Pd(4,4'-bpy)]_2[\alpha-SiW_{12}O_{40}]\}_\infty$  **5**.

lated to be 11.5 Å. The solvent accessible space of **5** was estimated to be 1951 Å<sup>3</sup>, which corresponded to 45 % of the unit cell volume. Thus, the spaces between the layers were considered to act as the guest sorption sites.

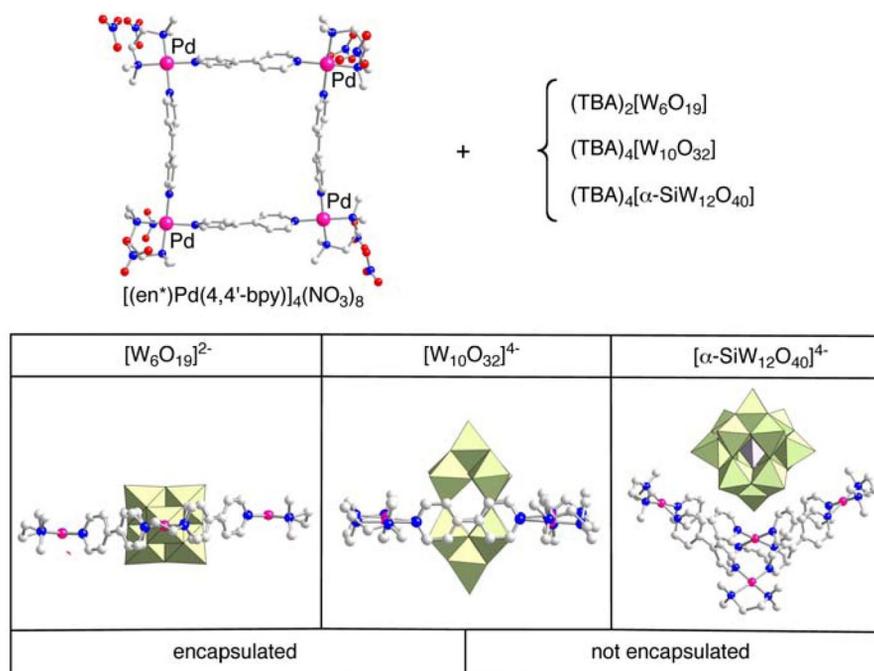
The guest-free state of compound **5** (**5'**) was formed by the removal of solvents of crystallization at 323 K under dry N<sub>2</sub>, the structure of which was characterized by the Rietveld analysis. When compound **5'** was treated with the vapor of hydrophilic organic molecules such as acetonitrile, acetone, 2-propanol, and dimethylsulfoxide (DMSO), the amounts sorbed were 3.3, 2.7, 1.4, and 1.7 mol mol<sup>-1</sup>, respectively, with slight expansion of the space between the layers. The regulated disposition of the ethylenediamine moieties between the layers probably played an important role in the sorption of the hydrophilic organic molecules. On the other hand, the hydrophobic molecules such as dichloromethane and hexane were excluded.

## ENCAPSULATION OF POMs BY SUPRAMOLECULES

Presynthesized cationic supramolecules could provide nanosized spaces for POMs and/or guest molecules inside the composites [24]. According to this idea, molecular triangle/square  $[(en^*)Pd(4,4'-bpy)]_n(NO_3)_{2n}$  [ $n = 3$  (triangle)/ $n = 4$  (square);  $en^* = N,N,N',N'$ -tetramethylethylenediamine] was synthesized [6].

The hybrid compounds of the molecular square and POMs were synthesized by the reaction of the molecular triangle/square with Lindqvist-type  $[W_6O_{19}]^{2-}$ ,  $[W_{10}O_{32}]^{4-}$ , and Keggin-type  $[\alpha-SiW_{12}O_{40}]^{4-}$  (Fig. 5). The reaction resulted in the formation of the corresponding hybrid compounds,  $\{[(en^*)Pd(4,4'-bpy)]_4[\square W_6O_{19}]\}[W_6O_{19}]$  [**6**],  $\{[(en^*)Pd(4,4'-bpy)]_4[\square W_6O_{19}]\}(NO_3)_6$  [**7**], a mixture of  $\{[(en^*)Pd(4,4'-bpy)]_4[\square W_{10}O_{32}]\}[W_{10}O_{32}]$  [**8**] and  $[(en^*)Pd(4,4'-bpy)]_4[W_{10}O_{32}]_2$  [**9**], and  $[(en^*)Pd(4,4'-bpy)]_4[\alpha-SiW_{12}O_{40}]_2$  [**10**] in moderate yields.

All compounds except for compound **10** retained the square structures of the cationic units. The edge distances [10.995(4)–11.189(2) Å] of the Pd square in compounds **6–9** were very close to those in



**Fig. 5** Encapsulation of molecular square  $[(\text{en}^*)\text{Pd}(4,4'\text{-bpy})]_4(\text{NO}_3)_8$  with POMs (POM =  $[\text{W}_6\text{O}_{19}]^{2-}$ ,  $[\text{W}_{10}\text{O}_{32}]^{4-}$ , and  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ ).

the molecular square. The diagonal Pd...Pd distances of compound **10** (15.1 and 12.7 Å) exhibited the highly distorted square structure. The Lindqvist-type  $[\text{W}_6\text{O}_{19}]^{2-}$  ( $9.9 \times 9.9 \times 9.9$  Å) and  $[\text{W}_{10}\text{O}_{32}]^{4-}$  ( $9.9 \times 9.9 \times 13.6$  Å) were encapsulated in the molecular square ( $13.8 \times 12.3$  Å), while the largest Keggin-type  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  ( $12.2 \times 12.2 \times 9.3$  Å) was not encapsulated. Thus, the encapsulation by the molecular square depended on the sizes of the POMs. There are several examples of the encapsulation of small,  $-1$  or  $-2$ -charged anions by the supramolecules [31–34]. In addition, POMs encapsulated by the supramolecular frameworks have been synthesized only under hydrothermal conditions [35–38]. Therefore, the present rational encapsulation of large  $-2$  or  $-4$ -charged POMs with the supramolecules under mild conditions is of importance.

## INCORPORATION OF NANOSIZED SPACES BY KINETIC CONTROL

All the results above show the construction and utilization of the intrinsic nanosized spaces within the crystal lattice. Since the thermodynamically stable single crystal does not always possess intrinsic nanosized spaces, methods to introduce nanosized spaces into dense nonporous single crystals are of importance. As stated in the introduction, a single crystal of  $(\text{NH}_4)_3[\alpha\text{-PW}_{12}\text{O}_{40}]$  grown at 473 K is nonporous (denoted as **11**). The single-crystal X-ray structure analysis of **11** showed a cubic cell (space group,  $Pn3\text{-}m$ ). The dodecahedron particle of **12** was formed by the equivalent planes of  $\{110\}$ . By decreasing the synthetic temperature from 473 to 298 K, spherical particles of 100–400 nm in size were formed (Fig. 1) (denoted as **12**). Compound **12** showed a large Brunauer–Emmett–Teller (BET) surface area of  $91 \text{ m}^2 \text{ g}^{-1}$  (pore diameter, 7–12 Å), suggesting that the spherical particles are aggregates of nanocrystallites of ca. 10 nm in size. The existence of nanocrystallites was confirmed by the high-resolution scanning electron microscopy (SEM) and atomic force microscopy (AFM) images. Based on these observations, the formation and growth mechanism of  $(\text{NH}_4)_3[\alpha\text{-PW}_{12}\text{O}_{40}]$  was suggested as follows: (i) formation of nanocrystallites, (ii) assembly of the nanocrystallites to form aggregates, and (iii)

growth of aggregates by the attachment of nanocrystallites [25]. The time courses of the turbidity of the synthetic solution, the concentration of the nanocrystallites, and the averaged particle sizes of  $(\text{NH}_4)_3[\alpha\text{-PW}_{12}\text{O}_{40}]$  were well reproduced by the calculation based on the mechanism. The decrease in the crystallinity and the increase in the porosity (BET surface area) by the decrease in the synthetic temperature from 473 to 298 K, could be explained by the increase in the rate constant of (iii), which probably disturbed the formation of epitaxial interfaces between the nanocrystallites. These results show the kinetic control of the self-organization process to change the morphology, crystallinity, and porosity of POM-based compounds.

## CONCLUSION

This review illustrates our concept and recent results of the hierarchical design of POM-based compounds with nanosized spaces. The use of cationic organometallic complexes or supramolecules directed the self-organization of the building blocks into regulated structures according to their size, shape, charge, and functional group to construct compounds with controlled pore size, pore volume, and hydrophilicity/-phobicity. The kinetic control of the self-organization process by the changes in the synthetic condition to form porous aggregates instead of nonporous single crystals was also presented. The following are the future goals to be achieved:

- Separation of enantiomers: The use of enantiopure organometallic complexes or supramolecules as building blocks would enable the construction of a homochiral framework in the POM-based compounds. The nanosized chiral space would realize the enantioselective inclusion and the separation of enantiomers from the racemic mixture [39].
- Catalysis in the nanosized space: The catalytic properties of POM can be controlled by the substitution of constituent atoms. For example,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  and  $[\gamma\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  can catalyze the epoxidation reactions of alkenes with high yields of epoxides and high efficiency of  $\text{H}_2\text{O}_2$  use [40,41]. A unique reaction would proceed by the confinement of POM and reactants in the nanosized space and/or by the cooperation of POM with the organometallic complexes and supramolecules.

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