

Synthesis of 3-D Ordered Macroporous $M_xH_{3-x}PW_{12}O_{40}$ ($M = Cs^+$ and NH_4^+): Trimodal Micro-, Meso-, and Macropores in $Cs_xH_{3-x}PW_{12}O_{40}$ Material

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3-D ordered macroporous (3DOM) crystalline $Cs_xH_{3-x}PW_{12}O_{40}$ and $(NH_4)_xH_{3-x}PW_{12}O_{40}$ were synthesized by a colloidal crystal template method. $Cs_xH_{3-x}PW_{12}O_{40}$ and $(NH_4)_xH_{3-x}PW_{12}O_{40}$ were deposited in the voids of templates by a two-step impregnation process and homogeneous precipitation, respectively, and polymer templates were removed by subsequent calcination. 3DOM crystalline $Cs_xH_{3-x}PW_{12}O_{40}$ exhibits trimodal micro-, meso-, and macroporosity.

In recent years, increasing attention has been paid to 3-D ordered macroporous (3DOM) materials with sub-micrometer pore size,¹ and these materials have been applied as photonic crystal materials, electrode materials, and catalysts.² Many kinds of 3DOM materials, including metal oxides, metals, carbon (materials), and polymers, have been successfully prepared by a colloidal crystal template method.¹

Heteropolyacids (HPAs) are widely utilized as catalysts in industrial processes, such as hydration, esterification, polymerization, and selective oxidation.³ HPA materials, especially cesium and ammonium salts of Keggin-type HPA, show a tertiary structure (aggregates of crystallites) in addition to the primary structure (molecular structure) and secondary structure (cubic crystal structure: packing of molecules) in their ionic crystals. Bimodal micro- and mesopores develop between the crystallites (tertiary structure): the micropores being formed between the crystal faces of the primary crystallites by crystallographic misfits and mesopores being formed between the aggregated crystallites.⁴

Although there has been much work on HPA supported on 3DOM materials,⁵ there has been only one report of 3DOM HPA. Zhang et al. reported fabrication of a 3DOM cesium salt of a Keggin-type phosphotungstate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ film.⁶ However, their $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was not a crystalline compound and had no micro- and mesopores. In the present study, we tried to synthesize 3DOM cesium and ammonium salts of Keggin-type phosphotungstates, $Cs_xH_{3-x}PW_{12}O_{40}$ (CsHPW) and $(NH_4)_xH_{3-x}PW_{12}O_{40}$ ((NH₄)HPW), bearing high crystallinity and a multimodal porous structure by a colloidal crystal template method.

3DOM HPA was synthesized by a colloidal crystal template of monodispersed poly(methyl methacrylate) (PMMA) spheres (diameter: 180 ± 8 nm).⁷ For the synthesis of 3DOM CsHPW, precursor solutions were impregnated in the PMMA template in two steps consisting of impregnation of $H_3PW_{12}O_{40}$ (HPW) solution and then Cs_2CO_3 solution.⁸ On the other hand, 3DOM (NH₄)HPW was synthesized by one-step homogeneous precipitation.^{4c,8}

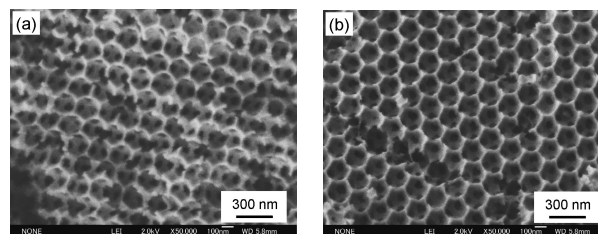


Figure 1. SEM images of the materials obtained after calcination at 723 K. (a) CsHPW and (b) (NH₄)HPW.

Figure 1 shows scanning electron microscopy (SEM) images of the obtained materials. In SEM images, 60–70% and 80% of the particles of CsHPW and (NH₄)HPW, respectively, display well-ordered 3DOM structures. In each case, pore sizes are ca. 144 nm and these values are ca. 20% smaller than the PMMA sphere diameter, mainly due to the shrinkage of PMMA spheres by melting.^{7b}

In order to maintain the 3DOM structure, acidity of HPW should be decreased. When only HPW solution was used as a precursor solution, 3DOM structures could not be obtained (Figure S1).¹¹ In the presence of strong acidic HPW, parts of the ester group of the PMMA are hydrolyzed to form poly(methacrylic acid) (PMAA),⁹ and the PMMA template could not retain its spheric form. Decrease in the acidity of HPW by the formation of cesium and ammonium salts in the voids decreased decomposition of PMMA (Figure S2),¹¹ and 3DOM structures were successfully obtained. (NH₄)HPW has 3DOM structures in the long-range compared to CsHPW whereas less PMAA was formed in the case of cesium salt (Figure S2),¹¹ indicating that reaction of HPW with Cs_2CO_3 in the second impregnation step caused inhomogeneous precipitation in the voids.

Figure 2 shows powder X-ray diffraction (XRD) patterns of the solids obtained after calcination at 723 K to remove the PMMA template. When only HPW solution was used as a precursor solution, HPW decomposed to $W_{12}PO_{38.5}$ (JCPDS 41-0369) (Figure 2g). In the case of CsHPW, a diffraction pattern typical for a cubic Keggin-type structure was observed (Figures 2b–2e). In general, thermal stability of HPAs is enhanced with increase in substitution of protons for Cs^+ , and the Keggin structure tends to be maintained after calcination.

However, HPW framework starts to decompose when Cs_2CO_3 amount exceeds quantity of $Cs/PW_{12}O_{40} = 3$, which is usual for HPW.¹⁰ Cs concentration in the second impregnation step should be lower than 0.1 M under our condition to obtain pure cubic CsHPA (Figures 2d, 2e, and Table S1¹¹). As Cs concentration increases more than 0.1 M, peak intensities of the

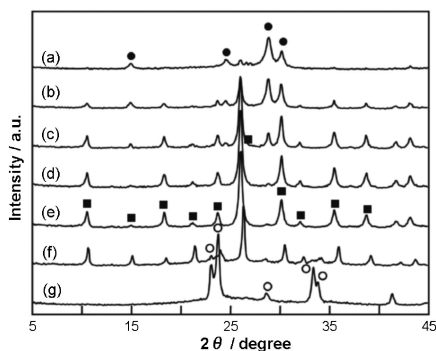


Figure 2. XRD patterns of the materials obtained after calcination at 723 K: CsHPW prepared using Cs_2CO_3 solution with cesium concentrations of (a) 0.6, (b) 0.3, (c) 0.15, (d) 0.1, and (e) 0.075 M, (f) $(\text{NH}_4)\text{HPW}$, (g) material prepared using only HPA solution. Closed square: cubic Keggin structure. Open circle: $\text{W}_{12}\text{PO}_{38.5}$ (JCPDS 41-0369). Closed circle: $(\text{Cs}_2\text{O})_{0.44}\text{W}_2\text{O}_6$ (JCPDS 47-0566).

by-product at 14.9, 28.9, and 30.2°, which typically corresponds to cesium tungsten oxide ($(\text{Cs}_2\text{O})_{0.44}\text{W}_2\text{O}_6$) (JCPDS 47-0566), become stronger (Figures 2a–2c). When Cs concentration is 0.6 M, Keggin structures are completely destroyed and only cesium tungsten oxide is formed (Figure 2a). These phenomena are observed in FT-IR spectra as well (Figure S3¹¹). Cs contents (x) of pure cubic $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ were calculated to be 2.3–2.8 by elemental analysis (Table S1¹¹).

In the case of $(\text{NH}_4)\text{HPW}$, diffraction peaks associated with cubic Keggin packing were observed (Figure 2f). However, $\text{W}_{12}\text{PO}_{38.5}$ (JCPDS 41-0369) is also formed as a by-product. Although the thermal stability of HPA is assumed to be increased by substitution of protons for NH_4^+ , the Keggin structure is partially destroyed after heating at 723 K. Absorption bands of HPAs and NH_4^+ at 1417 cm^{-1} are also observed from FT-IR spectra (Figure S3¹¹).

Figures 3 and S4 show N_2 adsorption isotherms of HPAs. Except for a Cs concentration of 0.6 M, the isotherms showed sharp uptake at the region of very low relative pressure, indicating the existence of micropores, and micropore volumes of these samples are different. The amount of uptake is comparable to the reported value (ca. 20 cm^3 (STP) g^{-1}).^{3a} When Cs concentration was 0.075 M, a small hysteresis loop was observed in the medium relative pressure range, and the obtained 3DOM $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ showed a large specific surface area (83 m^2g^{-1}). With increase in Cs concentration, micropores and mesopores disappeared and specific surface area decreased because of the formation of $(\text{Cs}_2\text{O})_{0.44}\text{W}_2\text{O}_6$ (Figure S4 and Table S1¹¹). These results suggest that $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ has micro, meso, and macroporous structures. Crystalline 3DOM materials have a skeleton structure consisting of strut-like bonds and vertexes.⁷ Their crystallite sizes calculated by Scherrer's equation from XRD data were ca. 20 nm, similar to diameters of strut-like bonds. We propose that the micropores are formed between crystallites by crystallographic misfits and that mesopores are formed in the vertexes where several crystallites aggregate.

Our 3DOM $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ showed catalytic activity for hydrolysis of ethyl acetate in excess water;¹¹ however, the reaction rate per weight of our material was lower (5.3 $\mu\text{mol g}^{-1}\text{min}^{-1}$) than the reported value (30.1 $\mu\text{mol g}^{-1}\text{min}^{-1}$)

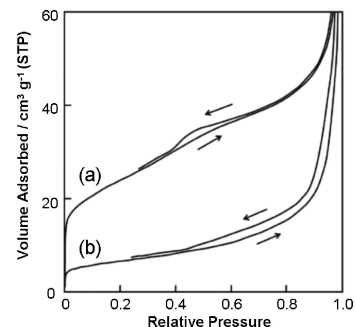


Figure 3. N_2 adsorption isotherms of the materials obtained after calcination at 723 K: (a) CsHPW prepared using Cs_2CO_3 solution with cesium concentration of 0.075 M and (b) $(\text{NH}_4)\text{HPW}$.

of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ with a large surface area (128 m^2g^{-1}).^{3b} Further study on application of 3DOM $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ as a catalyst is now underway.

In conclusion, 3-D ordered macroporous crystalline $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ were synthesized by a two-step impregnation process or homogeneous precipitation combined with a colloidal crystal template, respectively. Notably, the 3DOM $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ synthesized by this method has a specific pore structure consisting of trimodal micro-, meso-, and macropores.

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- General procedure: CsHPA; HPW (0.6 M as the concentration of protons) was dissolved in water–methanol solution ($\text{H}_2\text{O}/\text{CH}_3\text{OH} = 2/1$). A PMMA colloidal crystal template (1.0 g) was soaked in the solution at room temperature for 1 min. Excess solution was removed by vacuum filtration, and the filtrated solid was dried at 313 K overnight. Then the obtained solid was soaked in chilled water–methanol ($\text{H}_2\text{O}/\text{CH}_3\text{OH} = 2/1$) solution (2 mL) of Cs_2CO_3 (0.06–0.6 M as the concentration of Cs^+) for 3 min. Excess solution was removed by vacuum filtration in the same manner as above. $(\text{NH}_4)\text{HPA}$; 0.6 M HPW solution in water–methanol ($\text{H}_2\text{O}/\text{CH}_3\text{OH} = 2/1$), including 1.2 M (as the concentration of NH_3) urea, was infiltrated into voids of the PMMA colloidal crystal template for 1 min. Excess solution was removed by vacuum filtration. The solids were loaded into a quartz tube and calcined at 723 K under air flow according to the previous method.⁷
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