Synthesis of Hierarchically Meso-/Macroporous Titanium Tetraphosphonate Materials with Large Adsorption Capacity of Heavy Metal Ions

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Macroporous titanium tetraphosphonate materials with intraframework ethylenediamine groups and hierarchical mesostructure in the walls were synthesized by a simple surfactant-free process with the use of sodium salt of ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic acid), possessing large capacity for heavy metal ion adsorption with a preference sequence of $Cd^{2+} < Cu^{2+} < Pb^{2+}$.

In the course of the exploration of the mesostructured/mesoporous inorganic–organic hybrid materials for potential applications as sorbents, ion exchangers, ionic conductors, and catalysts, our efforts were directed towards the designed synthesis of new metal organophosphonate materials with hierarchically nanoporous structure. It has been known that the occurrence of multiscaled porosity is important and useful for catalysis and adsorption/desorption and for engineering of pore systems. The macropores incorporated in mesoporous materials could affect favorably the catalytic behavior by enhancing mass transfer and reducing diffusion resistance.[1] Metal phosphonates are important multifunctional materials owing to the combined properties from both inorganic species and organic groups, and the use of organophosphonate derivatives provides an almost unlimited ability to vary the organic component leading to variable modes of functionalization of the solid materials and possible control of the pore size.[2] By using terminal RPO_3 substituting groups, mesoporous phosphate/phosphonate of Ti, Zr,[3] and Al[4] were synthesized, but the phosphonate incorporation into the final materials is limited and restricted to the pore surface. Organically bridged diphosphonic acids ($(HO)_2OP–R–PO(OH)_2$) were then used to prepare mesoporous aluminum diphosphonates,[5,6] but only the alkylene-bridged groups were reported in the scanty publications, and the synthesis was performed mainly in the acid solution system. Titanium, vanadium, and oxide–phosphonate materials with very poor porosity were constructed from dendritic tetraphosphonates by nonhydrolytic condensation of water-insoluble arylphosphoric acid and metal alkoxide very recently.[7] In this letter, we report the preparation of titanium tetraphosphonate material with a hierarchically meso-macroporous structure, in which ethylenediamine groups incorporated in the framework walls, exhibiting efficient adsorption behavior for heavy metal ions.

Sodium ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonate) (EDTMPS) was used as organophosphorus coupling molecules for the synthesis of hierarchically meso-/macroporous titanium tetraphosphonate (Ti-EDTMPS). 3.404 g of titanium tetrabutoxide was added dropwise to 40 mL of an ethanol–water solution (1/3 of v/v) containing 3.06 g of EDTMPS (0.1 mol/L) under very gentle stirring at ambient temperature, and the pH value was around 8. After 24 h, the obtained mixture was sealed in a Teflon-lined autoclave and aged statically at 80 °C for 24 h. The product was filtered and dried overnight at 80 °C in an oven.

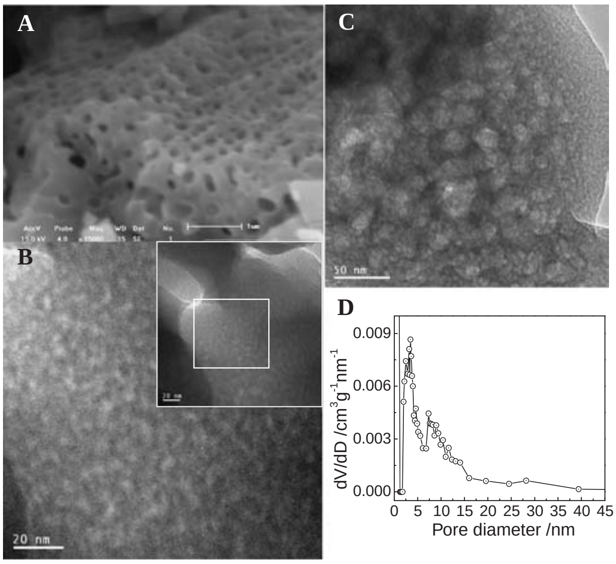

Figure 1. (a) SEM and (b), (c) TEM image of the synthesized meso-/macroporous Ti-EDTMPS. Low-magnification image of (b) is inserted. (d) BJH pore size distribution curve of the sample.

Figure 1 shows the SEM and TEM images of the resultant Ti-EDTMPS solid, revealing a hierarchically macro-/mesoporous structure presented in the irregularly shaped product particles of tens to several tens micrometers in size. A three-dimensional arrangement of uniform macroporous structure with pore sizes of hundreds nanometers (100–300 nm) is clearly observed from the SEM image (Figure 1a), which is further confirmed by the TEM image (Figure 1b). The walls between the macropores are mainly of 200–450 nm in thickness, composed of mesostructured pores of several nanometers in size with wormhole-like assembly in the area near the pore surface layers, revealed by the high-magnification TEM images. In the core part of the macroporous walls, under the particle/pore surface layers of small wormhole-like mesoporous structure, a novel mesocellular foam structure, similar to the previously reported mesostructured cellular foam (MCF) silica materials,[8] was seen (Figure 1c). Such an unusual hierarchical structure of titanium phosphonate, fabricated in the absence of the surfactant molecules, has never been reported. It is reminiscene of the biomineralization process of diatoms with intricate silica cell-wall architecture.[9] The hydrolysis of titanium tetrabutoxide precursor in the organophosphonate solution would result in the rapid formation of nanometer-sized titanium phosphonate sols, accompanying with the generation of a lot of butanol molecules. Meanwhile, in such a multiple component system of alkoxide–organophosphonate–alcohol (butanol, ethanol)–water, microemulsion drops are formed under mild stirring, and the Ti-EDTMPS sols aggregate along with the microemulsions to form the mesocellular foam structure. Some Ti-EDTMPS sols interact each other to form nanoclusters of several nanometers in size, which are mesostructured. At this stage, because of the presence of a large amount of butanol by-products, the reaction mixture become transferred to Ti-EDTMPS-based mesophases and water–alcohol domains by microphase separation,[10] induced by aging, leading to discrimination of them. This process proceeds to expand two- and three-dimensionally, ultimately resulting in the creation of hierarchical porous network. The BJH adsorption pore size distribution curve (Figure 1d) shows one narrow peak in the range of 2–5 nm, centered at 3.4 nm, and one broad distribution at 6–15 nm, which correspond to the wormhole-like mesostructure and mesocellular foam structure observed in TEM images, respectively. The surface area is low of only 15 m^2/g, possibly because of the existence of the organic species.

The FT-IR spectrum of Ti-EDTMPS shows the strong bands at 1048 and 1145 cm^{-1}, characteristic of phosphonate P–O···Ti stretching vibrations and P–CH_2N= groups,[11] respectively, and the shoulder peak around 988 cm^{-1} assigned to P–OH stretching vibrations, suggesting the presence of RPO_3H^-. The bands of 1435 and 1473 cm^{-1} could be assigned as P–C stretching vibrations and the C–H bending in –CH_2– groups connected with phosphorus, while the small bands at 1380 and 1320 cm^{-1} attributed to phosphoryl (P=O) frequency and C–N stretching, respectively. The ^{31}P MAS NMR spectrum shows two resonance signals of the phosphorus nuclei at 20 and 8 ppm, which could be assigned to P atoms of RPO_3H^- and RPO_3^{2-}, respectively. ^{13}C MAS NMR spectrum of the sample shows the somewhat broadened signal around 56 ppm, corresponding to the carbon atoms of nitrilomethylene and ethylenediamine in the framework of phosphonate groups. These data suggest that organophosphonate groups retain their integrity in the macro-/mesoporous solid. XPS data indicate the surface Ti/P ratio of 1.185, suggesting compositional homogeneity throughout the hybrid material.

Heavy metal ion adsorption studies were performed by treating 50 mL of homoionic solutions containing Cd^{2+}, Cu^{2+}, and Pb^{2+} ions of 10, 20, and 30 mg/L with 0.01 g of the macro-/mesoporous Ti-EDTMPS adsorbents for 3 h. UV–vis spectroscopy was used to assess the absorption capacity of samples for metal ions, and the results of the metal ion adsorption are summarized in Figure 2. The adsorption efficiency of the Ti-EDTMPS for Cd^{2+} ions ranged from 72.13 to 77.92%, for Pb^{2+} ions ranged from 84.62 to 90.91%, and for Cu^{2+} ranged from 83.33 to 85.85%, which are far higher than that of the macroporous pure TiO_2 prepared in the absence of organophosphonates. The selective complexation affinity sequence of metal ions is $Cd^{II} < Cu^{II} < Pb^{II}$.

The competitive adsorption experiment was also performed by treating 50 mL of a mixed ionic solution containing equal amounts (10 mg/L) of Pb^{2+}, Cu^{2+}, and Cd^{2+} with 0.01 g of Ti-EDTMPS. The adsorption efficiency of 28.34, 24.26, and 21.88% was obtained for Pb^{2+}, Cu^{2+}, and Cd^{2+}, respectively. This proved a distinct preference of the Ti-EDTMPS adsorbants for the uptake of Pb^{2+} ions compared to that of Cu^{2+} and Cd^{2+}, indicating that the synthesized hierarchical meso-/macroporous titanium phosphonate materials have an innate selective affinity for the adsorption of Pb^{2+} over Cu^{2+} and Cd^{2+}, which is comparable with the previously reported ethylenediamine-liganded mesoporous silica with a distinct preference for the uptake of Cu^{2+} ions over Ni^{2+} and Zn^{2+} [12] and the thiol-functionalized mesoporous silica that exhibited almost no affinity for Cd^{2+}, Pb^{2+}, Zn^{2+}, except for Hg^{2+}.[13]

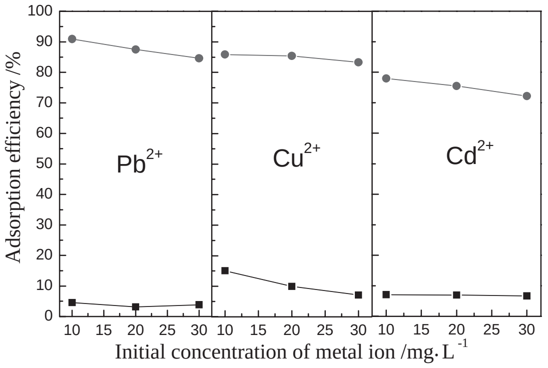

Figure 2. Metal ion adsorption efficiency for Ti-EDTMPS (—●—) and macroporous TiO_2 (—■—) materials.

In conclusion, the synthesis and characterization of the titanium tetraphosphonate materials with intraframework ethylenediamine functional groups and hierarchically meso-/macroporous structure have been demonstrated. The structural integrity of organically functionalized phosphonate groups was retained in the hierarchical Ti-EDTMPS, rendering the efficient adsorbents for heavy metal ions such as Cu^{2+}, Cd^{2+}, and Pb^{2+}.

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