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Organic–inorganic hybrid hierarchical aluminum phenylphosphonate microspheres

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ABSTRACT

Organic–inorganic hybrid phenylphosphonates with hierarchical morphologies have attracted much attention due to their structural versatility for various applications including catalysis, adsorption, and biomedicals, however, so far there have been no reports of the synthesis and application of aluminum phenylphosphonate microspheres. Here, we report a hydrothermal method for the synthesis of the flower-like porous aluminum phenylphosphonate microspheres by using phenylphosphinic acid and aluminum nitrate as the precursors. The nano-flakes formed in the initial growing stage are believed to play a key role in the formation of aluminum phenylphosphonate micro-flowers. The self-assembly of the flower-like microspheres has been identified to involve a two-stage growth process: a synergistic Ostwald ripening and oriented nanosheets attachment. The resultant aluminum phenylphosphonate micro-flowers can be easily converted to mesoporous amorphous aluminum phosphates by high temperature treatment without causing any morphology deterioration. The hierarchical aluminum phenylphosphonate microspheres have been applied to enrich peptide. This versatile synthesis method would enable to synthesize other metal phosphonates/phosphates spheres with interesting architecture for the potential application in catalysis, energy storage and nanomedicine.

1. Introduction

Construction of organic–inorganic hybrid materials is a rapidly expanding field of materials chemistry for the design of advanced materials with specific structure and functionality [1–3]. Metal phosphonate/diphosphonates as one such group of hybrid materials have attracted widespread interest because of their versatile applications in the areas of sorption, ion-exchange, catalysis, charge storage, and sensors [3–7]. In this connection, metal phenylphosphonates represent a particularly versatile field for investigation [8]. To date, the synthesis and application of various metal phenylphosphonates such as zirconium phenylphosphonate ($Zr(O_3PC_6H_5)_2$) [9], titanium phenylphosphonate ($Ti(O_3PC_6H_5)_2$) [10] and tin phenylphosphonate ($Sn(O_3PC_6H_5)_2$) [11] have been reported. One of the prototype metal phenylphosphonates is aluminum phenylphosphonate, $Al_2(O_3PC_6H_5)_3$, which is a layered compound with an interlayer spacing of 11.7 Å [12]. Impressive studies have been conducted on the synthesis of aluminum phenylphosphonate and aluminum phosphates due to their wide applications [12–15]. However, to the best of our knowledge, there has been no report on the synthesis of hierarchical spheres self-assembled by layered $Al_2(O_3PC_6H_5)_3$, which can provide the additional pores for accommodation of large bulk guest molecules without diffusion limitation to apply in adsorption, separation, catalysis and biomedicine.

Metal phosphate/phosphonate spheres and their porous structure have attracted increasing attention due to their unique properties, morphology and great potential applications [16–24]. For example, Li and his colleagues demonstrated the synthesis of transition-metal (Mn, Fe, Co, Ni, and Cu) phosphate colloidal spheres by low-temperature solution-phase reactions [16]. Protein-incorporated $Cu_3(PO_4)_2{\cdot}3H_2O$ microspheres and nanoflowers were prepared by using copper (II) ions as the inorganic component and various proteins as the organic component [17]. Besides, Clearfield and co-workers developed a hydrothermal method to synthesize $Sn(O_3PC_6H_5)_2$ with aggregated spherical shape [11]. Attempts have also been made to synthesize mesoporous spherical zirconium phosphonate and titanium phosphonate [18,20]. By contrast, no hierarchical aluminum phenylphosphonate spheres have been reported. The crystalline microporous aluminophosphate with zeolite properties has been known for their immense significance in the field of heterogeneous catalysis [25–30], in which aluminum adopted 4-, 5- and 6-coordination

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mode to form different active acid sites for catalytic reactions. Additionally, aluminophosphate molecular sieves can be easily doped with other metal ions to improve the framework properties. So, it is desirable to develop a reliable method to synthesize the hierarchically porous aluminum phenylphosphonate spheres and aluminum phosphates spheres. Their hierarchical structure will provide void space for entrapment and transport of biomolecules, and unsaturatedly coordinated aluminum will act as active sites for capture of biomolecules, also the doped heteroatom ions will improve the framework properties and provide additional metal ion affinity for biomolecules.

Here, we reported the synthesis of flower-like porous aluminum phenylphosphonate microspheres by using phenylphosphinic acid and aluminum nitrate as the precursors under acidic condition. As a result, new types of porous organic–inorganic hybrids consisting of aluminum phenylphosphonate layered structures and spherical morphology have been obtained for the first time. The size and morphology of the resultant aluminum phenylphosphonates could be modulated by varying the reaction time. Moreover, the mechanism of the self-assembly process to form the flower-like microspheres is discussed in detail. By calcinations of these porous aluminum phenylphosphonate microspheres, mesoporous amorphous aluminum phosphate micro-flowers with uniform pore size of ~5.5 nm can be prepared. For an application demonstration, the hierarchical aluminum phenylphosphonate microspheres have been assessed as a candidate material for peptide enrichment.

2. Experimental section

2.1. Chemicals and reagents

All materials were of analytical grade and used as received without any further purification. phenylphosphinic acid (PPA, $C_6H_7O_3P$, 99%), aluminum nitrate nonahydrate, ($Al(NO_3)_3{\cdot}9H_2O$, $\geqslant$98%), α-cyano-4-hydroxycinnamic acid (CHCA, $\geqslant$99%, matrix use only), trifluoroacetic acid (TFA, $\geqslant$99%), acetonitrile (ACN, $\geqslant$99%) and proteins/peptides were purchased from Sigma–Aldrich. Other reagents were purchased from ShangHai Chemical Reagent. Inc. of Chinese Medicine Group.

2.2. Synthetic procedure

Flower-like porous aluminum phenylphosphonate microspheres were synthesized by using $C_6H_7O_3P$ and $Al(NO_3)_3{\cdot}9H_2O$ as the precursors under acidic condition. In a typical synthesis, 7.5 mL of 0.04 M $C_6H_7O_3P$ was added into a HNO_3 solution (0.035 M) containing 7.5 mL of 0.04 M $Al(NO_3)_3{\cdot}9H_2O$, then, 0.44 mL of 1.5 M sodium hydroxide (NaOH) solutions was added into the above solution to tune the pH value to 1.6. The mixture was stirred for 30 min until a homogeneous solution was formed, and the resulted solution was transferred into a Teflon-lined autoclave and heated for 19 h at 100 °C under static conditions. The solid products were collected by centrifugation and washed with distilled water, respectively. The aluminum phenylphosphonates were denoted as AlPP-*n*, where *n* (*n* = 0.75, 1, 1.25, 2, 5, 19, and 72) is the hydrothermal treatment time at 100 °C.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an Empyrean powder diffraction system using Cu Kα radiation of 0.15406 nm wavelength. The nitrogen sorption experiments were performed at 77 K on a Micromeritics ASAP 3000 system. Prior to the measurement, the samples were outgassed at 120 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using adsorption data at the relative pressure range of P/P_0 = 0.05–0.25. Pore size distributions were calculated from adsorption branch using the Barrett–Joyner–Halenda (BJH) method. The total pore volumes were estimated from the amounts adsorbed at a relative pressure (P/P_0) of 0.99. High resolution scanning electron microscopy (HRSEM), field-emission scanning electron microscopy (FESEM) and scanning electron microscopy (SEM) were undertaken on a HITACHI S-5500, HITACHI SU 8010 and JSM 6360 LV microscope operating at an accelerating voltage of 1–30 kV, respectively. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 at an acceleration voltage of 120 kV. FT-IR spectra were collected with a TENSOR 27 IR spectrometer in the range of 4000–400 cm^{-1} using KBr pellet. ^{13}C (100.5 MHz) cross-polarization magic angle spinning (CP-MAS), ^{31}P (161.8 MHz) and ^{27}Al (79.4 MHz) MAS solid-state NMR experiments were recorded on a BRUKER DRX 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. ^{13}C signals were referenced to tetramethylsilane, ^{31}P NMR signal was referenced to H_3PO_4 (85 wt%). The experimental parameters were 6-kHz spin rate, 2-s pulse delay, 6-min contact time, for ^{13}C CP-MAS NMR experiments; 8-kHz spin rate, 3-s pulse delay, 10-min contact time for ^{31}P MAS NMR experiments. Thermal analysis (TGA and DTA) was carried out in air on a Perkin–Elmer Pyris Diamond TG-DTA 6300 at a heating rate of 5 °C min^{-1} from room temperature to 800 °C.

2.4. Enrichment tests

Enrichment tests toward peptides and proteins were performed, where the low concentrated solutions were prepared through a step-wise dilution manner. The microspheres were dispersed in water at a concentration of 10 mg/mL and 10 μL of the slurry was directly added to the prepared solutions. Then the supernatant was removed by centrifugation after 10 min enrichment and the microspheres were collected. For matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI TOF MS), the microspheres were incubated with 1 μL of matrix solution (10 mg/mL CHCA in TFA/ACN/water, 0.1%/49.9%/50%, v/v/v) and analyzed on the plain steel MALDI plate. The MS spectra were collected accumulating 500 laser shots at 10 different spots on Bruker Autoflex II Smartbeam system and no smooth spectra were used.

3. Results and discussion

3.1. Aluminum phenylphosphonate flower-like microspheres

Self-assembling in the form of aluminum phenylphosphonate flower-like microspheres was prepared by the reaction of equimolar amounts of phenylphosphinic acid (PPA) and aluminum nitrate (in a 1:1 molar ratio); NaOH solutions were then added to tune the pH value to 1.6. The morphology of the resultant aluminum phenylphosphonates (AlPP-*19*) with hydrothermal treatment 19 h was characterized by scanning electron microscopy (SEM) and transaction electron microscopy (TEM) with the results shown in Fig. 1. As can be seen from Fig. 1a, uniform and well-dispersed flower-like aluminum phenylphosphonate microspheres with an average diameter of 8 μm are observed. A SEM image (the left in Fig. S1) with a large amount of visible microspheres was also obtained in order to measure the particle size of aluminum phenylphosphonate microspheres. The diameter of aluminum phenylphosphonate microspheres was observed in the range of 5–13 μm and the maximum distribution located at 8 μm as shown in the right of Fig. S1, which can further confirm that the size of microspheres is