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Synthesis of mesoporous hydroxyapatite using a modified hard-templating route

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1. Introduction

Recently, much attention has been attracted by mesoporous materials due to their high surface areas, large and tunable pore size, and large pore volumes, which are crucial for developing new types of catalysts, adsorbents, drug delivery system, and so on [1,2]. Therefore, many efforts have been placed on the synthesis of mesoporous materials [3–5]. In 1992, Kresge et al. [3] successfully developed a supermolecular templating technique, which could be used to prepare silicon based mesoporous materials. After that, Kim et al. [4] reported the first synthesis of a new type of mesoporous carbon molecular sieve by carbonizing sucrose inside the pores of the MCM-48 mesoporous silica molecular. The above two routes demonstrated two kinds of typical strategies used as the synthesis of mesoporous materials, which can be designed as "soft-templating" and "hard-templating" routes, respectively.

Hydroxyapatite-calcium, $Ca_{10}(PO_4)_6(OH)_2$ (denoted as HAP) is a famous bioceramics materials due to its good biocompatibility, excellent ability to form chemical bond with living bone issue, and suitable osteoconductivity [6,7]. Moreover, HAP with various morphologies and surface properties have also been investigated as drug carriers for the delivery of a variety of pharmaceutical molecules because of its nontoxic and noninflammatory properties [8]. Considering the numerous applications of HAP, different morphologies HAP materials in the form of ceramics body [9], nanostructure [10], uniform porous [11]

ABSTRACT

Mesoporous polycrystals of hydroxyapatite-calcium are synthesized via a modified hard-templating route. The structure properties of hydroxyapatite-calcium are characterized by means of X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and N₂ adsorption-desorption isotherms. Wide-angle X-ray diffraction and Fourier transform infrared spectroscopy measurements reveal that the crystalline grains consist of highly crystalline pure hydroxyapatite phases. Transmission electron microscopy results show that rod-like hydroxyapatite-calcium grains with an average diameter of about 100 nm long and about 20 nm wide are uniformly distributed, which are also observed with an average pore size of 2–3 nm. Based on N₂ adsorption-desorption isotherms investigation, the pore size, surface area and pore volume of mesoporous hydroxyapatite-calcium are 2.73 nm, 42.43 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively.

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and mesoporous [12] structure have been widely reported. Among them, mesoporous HAP has attracted more attention, thus, design and development on synthesis method becomes a hot issue [12–14]. In this paper, we demonstrated a novel modified "hard-templating" route used as the synthesis of mesoporous HAP. We adopted the SBA-15 template and organic carbon sources as the starting materials, and they can be used to prepare ordered mesoporous carbon with two-dimensional hexagonal structure, CMK-3, according to the reported technique [15]. Then, mesoporous HAP was successfully synthesized utilizing CMK-3 as hard template, which accorded with the removal of carbon templates by combustion (600 °C/air, 8 h).

2. Experimental

2.1. Materials and synthesis procedure

All the reagents including CaCl₂·2H₂O (A.R.), (NH₄)₂HPO₄, NaOH (A.R.), H₂SO₄ (A.R.) and sucrose (A.R.) were received without further purification. High-quality SBA-15 was obtained from Zhao et al. [16], which was prepared according to their previously reported method. Fig. 1 shows the flow sheet of the procedure used for the preparation of mesoporous HAP. Firstly, CMK-3 was synthesized by SBA-15 as a silica template and sucrose as a carbon precursor following the previously reported recipe [15], except for the following modifications. The carbonization was completed by pyrolysis with heating to typically 1173 K under N₂ atmosphere. The carbon–silica composite obtained after pyrolysis was washed with 1 M NaOH solution (50 vol.% ethanol–50 vol.% H₂O) twice at 373 K, to remove the silica template. The template-free carbon

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Fig. 1. The formation procedure of mesoporous HAP in this work.

product thus obtained was filtered, washed with ethanol, and dried at 393 K. Secondly, mesoporous HAP was prepared; by a modified "hard-templating" route, together with the refluxing wet chemical method. In a typical process, stoichiometric amounts (Ca/P = 1.67) of CaCl₂ (2.9406 g CaCl₂·2H₂O dissolved in 60 ml deionized water [DW]) was added dropwise to a solution of (NH₄)₂HPO₄ (1.5847 g) and 0.36 g as-prepared CMK-3 dissolved in 120 ml DW; the pH was adjusted to 10–11 using 2 M NaOH, yielding a milky suspension, which was refluxed at 120 °C for 24 h. The final suspensions were aged for 12 h at room temperature, filtered and thoroughly washed with DW. The recovered gray precipitate was dried at 100 °C for 12 h in an oven, and then sintered at 600 °C for 8 h in air to remove the carbon templates. Finally, a white and fluffy-like mesoporous HAP was obtained.

2.2. Characterization

The wide-angle X-ray diffraction pattern was recorded by using a SHIMADZU model XRD-6000 X-ray powder diffractometer (Cu K α radiation, 40 kV, 30 mA and a scanning speed 2.0° (2 θ)/min). Fourier transform infra-red (FT-IR) spectrum was collected on a FTIT-AVATAR370 spectrophotometer over the range of wavenumber 2000–400 cm⁻¹, and the standard KBr pellet technique was employed. Transmission electron microscope (TEM) images were recorded on a JEOL-2010 Electron Microscope with an acceleration voltage of 120 kV. N₂ adsorption/desorption analysis was performed at 77 K using a Quantachrome Quadrasorb SI apparatus. The specific surface area was determined by the Bruaauer– Emmett–Teller (BET) method using the data between 0.05 and 0.3. The pore parameters (pore volume and pore diameter) were



Fig. 2. XRD pattern of mesoporous HAP calcined at 600 °C.

evaluated from the desorption branch of isotherm based on Barrett–Joyner–Halenda (BJH) model.

3. Results and discussions

3.1. XRD and FT-IR analysis

Fig. 2 shows the typical diffraction peaks of HAP, especially the three strongest peaks of HAP at $2\theta = 25.8^{\circ}$, 31.8° and 32.9° , which can be indexed as (002), (211) and (300), respectively, according to the standard data [17]. The XRD pattern reveals that the structure of as-synthesized HAP belongs to the hexagonal $P6_3/m$ space group with lattice constant of a = 9.418 Å and c = 6.884 Å. It also testified that the present "hard-templating" route, together with the refluxing wet chemical method can obtain pure HAP phase. Further, Fig. 3 shows the FT-IR spectrum of the calcinated HAP sample. Phosphate absorption bands $[v(PO_4^{3-})]$ occur at about 1031, 959, 606 and 564 cm⁻¹, and a hydroxide absorption band $[v(OH^{-})]$ is observed at about 3436 cm⁻¹, which are all characteristic for a typical HAP FT-IR spectrum [18]. In addition, as shown by the enlarged view of the FT-IR spectrum in the range of 500 and 700 cm^{-1} in the inset, we can obviously find the fine bands at 606 and 564 cm⁻¹, which are ascribed to the triply degenerated v_4 vibration of O–P–O bond.

3.2. TEM and NADI investigations

Fig. 4 presents the typical TEM images of as-synthesized mesoporous HAP with different scale. It can be seen from Fig. 4(a) that rod-like HAP grains with an average diameter of



Fig. 3. FT-IR spectrum of as-synthesized mesoporous HAP calcined at 600 $^{\circ}$ C, the inset shows the enlarged FT-IR spectrum in the range of 500 and 700 cm⁻¹.



Fig. 4. Typical TEM images of mesoporous HAP calcined at 600 °C: (a) 100 nm scale and (b) 20 nm scale.



Fig. 5. N_2 adsorption-desorption isotherms for mesoporous HAP calcined at 600 °C, inset: pore size distribution of mesoporous HAP based on nitrogen absorption analysis.

about 100 nm long and about 20 nm wide are uniformly distributed and the morphology of HAP samples are well-defined. Moreover, there are many pores dispersed on the rod-like HAP grains. Further, Fig. 4(b) gives the TEM images of mesoporous HAP in 20 nm scale, which can be used to observe the morphology of HAP samples in a facile way. It is found that most pores are of irregular quadrilateral shape with an average pore size of 2–3 nm.

The detailed parameters of the pores dispersed on the rod-like HAP grains were determined by N_2 adsorption-desorption

isotherms method. Fig. 5 shows a typical N₂ adsorption–desorption isotherms for mesoporous HAP calcined at 600 °C, which exhibit a mesoporous materials type IV curve with a hysteresis loop. The pore size distribution calculated from the adsorption branch of the isotherms based on BJH model was shown in the inset of Fig. 5. As is shown in the inset of Fig. 5, most of the pore size is distributed around 2.73 nm. Besides, based on overall investigation on the N₂ adsorption–desorption data, we can find that surface area and pore volume of mesoporous HAP in this work is 42.43 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively. We can find that mesoporous HAP prepared by the present "hard-templating" route has excellent application properties with large surface areas and small pore size, which can be promising as catalysts, absorbents, separation, and host materials.

3.3. Discussion

Here, we will discuss the formation mechanism of mesoporous HAP. In this work, we adopted a modified hard-templating route to prepare mesoporous HAP materials. Fig. 6 gives the involved experimental process and possible mechanism describing the formation of mesoporous HAP. The structure of the CMK-3 carbon is exactly an inverse replica of SBA-15, and we adopted the similar method to inversely replicate CMK-3, and prepare mesoporous HAP. As is reported in many references [15,19], the structure of SBA-15 consists of the hexagonal arrangement of cylindrical mesoporous tubes, and CMK-3 is the ordered arrangement of the carbon nanorods. So we can expect that mesoporous HAP will form the similar mesoporous tubes are obtained in our experiments, and the possible reasons can be ascribed to the complicated aqueous system in the refluxing process.



Fig. 6. The experimental process and possible mechanism describing the formation of mesoporous HAP in this work.

4. Conclusions

Mesoporous polycrystals of hydroxyapatite-calcium are synthesized via a modified hard-templating route in the present work. Ordered mesoporous carbon CMK-3 was formed through SBA-15 template and organic carbon sources. Mesoporous hydroxyapatite-calcium was successfully synthesized utilizing CMK-3 as hard template, with the removal of carbon templates by combustion (600 °C/air, 8 h). The structure properties of the hydroxyapatite-calcium phase are characterized by powder X-ray diffraction and Fourier transform infrared spectroscopy. Transmission electron microscopy results show that rod-like hydroxyapatite-calcium grains about 100 nm long and about 20 nm wide are uniformly distributed, with an average pore size of 2–3 nm. Based on overall investigation on the N₂ adsorption–desorption data, the pore size, surface area and pore volume of this material was found to be 2.73 nm, 42.43 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively.

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