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Preparation of pore expanded mesoporous hydroxyapatite via auxiliary solubilizing template method

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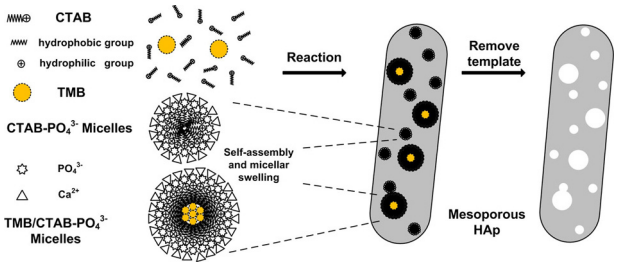
HIGHLIGHTS

- CTAB and TMB were used as soft template and pore expanding agent, respectively.
- Average length of the as-synthesized HAp nanoparticles is 50–150 nm.
- Large amount of mesoporous spread around the surface of mesoHAp nanorods.
- The shape of mesopores was elongated and opened at both extremities.
- Pore diameter of mesoHAp was up to 15 nm, indicating the pore enlargement of TMB.

GRAPHICAL ABSTRACT



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ABSTRACT

Here we present a facile approach to prepare pore-expanding mesoporous hydroxyapatite (mesoHAp) using solubilized micelle template. 1,3,5-rimethy benzene (TMB) was selected as auxiliary solubilizer together with the general soft template cetyltrimethylammonium bromide (CTAB). Enlarged mesoporous can be obtained through the swelling of micelle. Numerous individual nano channels can be observed under TEM images spreading and penetrating within the mesoHAp nanorods. Compared to the mesoHAp without TMB, the channels have enlarged dimensions of about 5–15 nm and the space between the nano channels are filled with an ordered crystalline HAp structure with typical hexagonal crystals. A probable mechanism is that TMB can enter into the amphiphilic CTAB micelle to form swelled TMB/CTAB-PO_4^{3-} complex, and in the presence of Ca^{2+}, $Ca_9(PO_4)_6$ clusters are preferentially condensed on the micelle surface due to the conformation compatibility between the identical hexagonal shapes of the micelles and $Ca_9(PO_4)_6$. Interesting, the pore size distribution of mesoHAp was centered at ~4.7 nm and ~10 nm, which might be arisen from the coexistence of both unsolubilized CTAB micelles and solubilized TMB/CTAB micelles. The pore-enlarged mesoHAp nanoparticles presented a platform for protein delivery system and might be applicable in biocomposite scaffold for bone regeneration.

1. Introduction

Recently, the synthesis of inorganic mesoporous materials has attracted much attention in chemistry and materials communities because of their low density, large specific area and pore volume, small size, mechanical and thermal stabilities, and surface permeability [1–3]. Up to now, a variety of mesoporous materials have

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been developed including the representative mesoporous silica-based molecular sieves, such as SBA and MCM. As one of the most energetic research areas in materials science [4], mesoporous silica-based nanoparticles (MSNs) have variety of potential applications in cosmetic, catalysis, coatings, composite materials, dyes, ink, artificial cells and fillers [5–8], etc. Despite the hot topic, silica-based mesoporous materials may not be suitable for tissue regeneration *in vivo* since its vague biological response.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), the major inorganic component of bone and teeth, is a key biomaterial in potential orthopedic [9], dental, and maxillofacial therapies because of the excellent biocompatibility, bioactivity, and osteoconductivity [10–13]. Moreover, it is worth noting that mesoporous HAp (mesoHAp) nanoparticles have greater potential in drug delivery systems, due to the distinct advantages of highly ordered mesoporous structure, large surface area and porosity that provide excellent loading capacity and releasing profile. Therefore, mesoHAp can be incorporated into scaffolds for the beneficial effects of improving osteogenesis and delivery of biologically active molecules [14].

However, despite their favorable properties, fabrication of mesoHAp with higher surface area is difficulty owing to its preferable crystallization in aqueous solution and then cannot interact with surfactant molecules. According to the literature, most of mesoporous calcium phosphate has the surface areas of 20–60 m^2g^{-1}. Another challenge lies in the relative smaller pore diameters less than 5 nm [15], whereas most cytokines are 8 nm or larger [16–18]. Therefore, a number of studies have been focused on the improvement of the pore diameter of mesoHAp [16,19,20].

Various techniques have been utilized to fabricate mesoHAp, including sol–gel method [19], hydrothermal method [16], microemulsion process [20] and co-precipitation technique [21], there into the templating method is regarded as the most valid approach to obtain mosoHAp. A series of surfactants, including pluronic P123 [22,23], sodium dodecyl sulfate (SDS) [24], non-ionic block co-polymer pluronic F127 [25,26] and cetyltrimethylammonium bromide (CTAB) [15,27], have been used as templates for synthesis of mesoporous materials. For example, Coelho et al. [27] synthesized HAp nanorods using CTAB and the effect of the sintering temperature on its nanostructure was studied. Li et al. [15] synthesized HAp using CTAB and studied the impact of reaction temperature and CTAB/PO_4^{3-} ratio on its thermostability. However, most of these studies are focus on the improvement of stability of HAp, the efficient strategy of mesoporous pore size enlargement is still defective. Therefore, synthesis of large pore size mesoHAp is an extremely promising research.

In recent research of ordered mesoporous siliceous materials, additional organic molecules have been appended to the template to achieve pore-expanding [28]. Inspired by this method, an alkylated benzene hydrocarbons, 1,3,5-trimethy benzene (TMB) is involved combined with the general soft template CTAB. The auxiliary TMB is conductive to the enlargement of pore diameter of mesoHAp through the micellar solubilization. The physicochemical properties are investigated, and the possible mechanism of pore size expanding is proposed.

2. Experimental

2.1. Materials and synthesis procedure

The procedure employed for the synthesis of HAp nanorods was as follows and all reagents were of analytical grade, purchased from Shanghai Chemical Co., Ltd., PR China and used with no further purification. In a typical procedure, 5.48 g of $K_2HPO_4{\cdot}3H_2O$, 8.74 g of CTAB, and 2.88 g of TMB were dispensed in deionized water to form 100 mL solution 1 (1 M sodium hydroxide solution was used to adjust the pH to 12). Then, 4.44 g of $CaCl_2$ was directly added into 60 mL H_2O to form solution 2. After vigorously stirring and ultrasonication respectively until optically transparent, solution 2 was introduced into the well-dispersed solution 1drop by drop. The reactant molar ratio of Ca^{2+}/PO_4^{3-} was kept at 1.67. After additional agitation at ambient temperature and normal atmospheric pressure for 3 h, the as-obtained mixing solution was refluxed at 120 °C for 48 h to remove the template of CTAB and TMB, followed by cooling to room temperature naturally. Finally, the precipitate was separated by centrifugation and washing with deionized water and ethanol for six times repeatedly, and dried in vacuum at 60 °C for 24 h, then calcined in a furnace at 550 °C for 6 h to obtain the final mesoHAp (denote as S3). The samples synthesized without TMB (denote as S2) and without template (nHAp, denote as S1) were used as control.

2.2. Characterization

The wide-angle (θ from 10 to 100°) and small-angle (θ from 0 to 5°) XRD patterns were recorded by using a SHIMADZU model XRD-6000 X-ray powder diffractometer (Cu Kα radiation, 40 kV, 30 mA and a scanning speed 2.08 (2μ)/min). Fourier transform infra-red (FTIR) spectrum was collected on a FTIT-AVATAR370 spectrophotometer over the range of wavenumber 4000–300 cm^{-1} using KBr pellet. Morphologies were examined via a field-emission-type scanning electron microscope (FSEM, SIRION-100). Transmission electron microscope (TEM) images were obtained on a JEOL-2010 Electron Microscope with an acceleration voltage of 120 kV N_2 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, the pore parameters (pore volume and pore diameter) were evaluated from the desorption branch of isotherm based on Barrett–Joyner–Halenda (BJH) model.

3. Results

3.1. X-ray diffractions

The wide-angle XRD patterns of the obtained samples (S1, S2 and S3) were shown in Fig. 1A. All the diffraction peaks of the three samples corresponded to the standard characteristic peaks of HAp (JCPDS card: No. 24-0033), indicating that the phase of the samples was highly pure HAp. Small-angle ($2\theta < 5°$) XRD diffraction was used to verify the existence of long-range ordered structure inside the samples [26]. As shown in Fig. 1B, S1 exhibited a smooth curve compared to S2 and S3. However, numerous peaks and background appeared in the XRD pattern of S2 and S3, especially from 2 to 4°, indicating irregular mesoporous structures existed in S2 and S3. Furthermore, no significant difference was observed between S2 and S3 from Fig. 1B.

3.2. FT-IR spectroscopy

Fig. 2 shows the FTIR spectra of the three samples. For S3, phosphate absorption bands occurred at 474, 563, 964, 1032 and 1092 cm^{-1}, and the hydroxyl absorption bands at 3572 and 634 cm^{-1} were characteristic of a typical characteristic absorptions of hydroxyapatite [29]. The peaks at 3433 and 1639 cm^{-1} were assigned to the bending mode of the adsorbed water [30]. The two sharp and weak peaks at 721, 2854 and 2924 cm^{-1} were attributed to the residual of CTAB [17]. No trace of TMB was observed from the FTIR spectra, indicating TMB was removed cleanly after the high temperature refluxing, repeated washing and calcining.