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Solvothermal synthesis of hydroxyapatite nanorods with assistance of green polymer

Hui Yang [a,*], Tongxiang Liang [a], Xiaopeng Qi [a], Honghui Jiang [a], Yiqun Deng [a], Ping Wang [a], Huichang Gao [b]

[a] School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China
[b] School of Medicine, South China University of Technology, Guangzhou 510641, China

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ABSTRACT

Development of low cost, environmental friendly crystal growth modifying reagents that are effective to HAp's microstructure regulation is highly crucial. Herein, sodium lignin sulfonate (SS), a byproduct of the pulp process, was used for preparing HAp nanorods. Results showed that both stirring time of reaction solution and the concentration of SS affected crystals' structure and aspect ratio. The growth mechanism was discussed on the basis of the results. And we hope this new synthetic strategy will offer an attractive route for the design of functional HAp nano−/micro- materials with fine structure.

1. Introduction

In the past decades, nanostructure processing is a key issue in achieving materials with fine structure [1,2]. Among them, hybrid materials and inorganic materials with controllable size and morphology are upcoming materials for drug delivery [3], therapy [4], sensors [5], etc. As the main inorganic constituents of bones in vertebrates, hydroxyapatite (HAp) attracts much attention because of its excellent biocompatibility, bioactivity and osteoconductivity [6,7]. Therefore, synthetic HAp nano/micro- particles is a promising candidate for bone tissue repairing. Although the nanostructure of HAp is closely associated with its physicochemical properties, it's still a big challenge to synthesis HAp nanoparticles with well defined morphology. Hence, significant research efforts have been devoted to prepare HAp materials with various structures, such as microspheres [8], microflowers [9], nanospheres [10], nanowires [11] and nanorods [12]. Among them, HAp nanorods are very promising for applications in various fields. Interesting, HAp nanorods in bones and teeth endows these tissues unique mechanical properties [13]. Up to now, HAp nanorods have been obtained through variety of methods including hydrothermal mode, microwave-assisted synthesis, hard and soft template techniques [14–16]. Inspired by biomineralizaion process, soft template techniques are highly effective in preparing HAp nanorods.

In soft template regulation process, synthetic surfactants, used for preparing materials with fine structure, bring about several problems, such as high cost, potential toxicity and difficult to remove because of hydrophobic property. Therefore, a proper modulator with low cost, water soluble and environmental friendly properties should be applied. Lignin, which is antioxidant, antimicrobial, biodegradable and environmental friendly, is the second most abundant natural polymer on earth next to cellulose. Till now, intense efforts are being made to use lignin as a reinforcement constituent to improve the flexibility of HA coating on the metallic substrate [17]. Although there is a wide range of hydroxyl groups in the structure of lignin, because of low affinity between hydroxyl groups and HA crystal nucleus, few researchers apply it to control the nucleation, growth, size distribution and shape of HA. As a derivative lignin, SS also derives from natural plants, and it's a byproduct of the pulp process. Moreover, high affinity between Ca^{2+} and sulfonic group ensures the interaction between HA and SS, which provides nucleation sites for HA, and regulates the growth and self-assemble of nanocrystals, and might results in the formation of HA nanorods [18].

Herein, HAp nanorods were successfully obtained with the aid of SS at hydrothermal system. The interaction between lignin sulfonate and HAp was investigated, and the resulted products were characterized by TEM, SEM, XRD and FT-IR.

2. Materials and methods

2.1. Sample preparation

All chemical were of analytical grade reagents, and purchased from Aladdin, unless otherwise stated, these reagents were used without further purification. In a typical synthesis, 0.15 g SS was dissolved into

* Corresponding author.
E-mail addresses: yanghui_2521@163.com (H. Yang), gaohuichang1986@163.com (H. Gao).

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40 ml de-ionized water, and 2.9518 g $Ca(NO_3)_2 \cdot 4H_2O$ was added, the solution was stirring for 1 h, then 10 ml solution containing 0.99 g $(NH_4)_2HPO_4$ was added. Through controlling the stirring time of the mixture, the final structure of the particles could be modified. After that, the mixture was transferred into a stainless steel autoclave, sealed and heated at 160 °C for 24 h. Then the solution was cooled naturally, and the precipitates were washed with de-ionized water several times, centrifuged and then dried at 70 °C for 12 h.

2.2. Characterization

The microstructure of the samples was analyzed using scanning electron microscopy (SEM, Zeiss Sigma) and transmission electron microscopy (TEM, JEOL-2010) with an acceleration voltage of 120 kV. The crystalline phase was characterized with X-ray diffraction, carried out with a PANalytical PRO X-ray diffractometer using Cu Kα (λ = 0.15418 nm) radiation. Fourier Infra-Red (FT-IR) spectra have been obtained in the range of 4000–500 cm^{-1} using Bruker Vector 33 with a resolution of 0.3 cm^{-1}.

3. Results and discussion

HAp nanorods with dimensions ~50 nm has been successfully synthesized, the corresponding TEM and HRTEM images are shown in Fig.1a and b, respectively. TEM results showed nanorods is uniform and packed with each other. The lattice fringe gives an interplanar spacing of 0.344 nm, that corresponds to that of the (002) lattice planes of HAp. FTIR result shows small amount of –COO appears, that might be assigned to the participation of CO_2 in air [19]. Besides, XRD spectra reveals the sample is single-phase (JCPDF Card No. 73–0293), and no peaks of impurities have been detected. What's more, compared with the relative intensity of (002) in standard pattern, the corresponding peak's intensity of the sample is obvious higher, along with the HRTEM result, we believe that this should be ascribed to the preferred orientation growth along c axis.

Then, we investigated the effect of SS on the final structure of the HAp particles. As shown in Fig. 2, when the initial concentration of SS was 0.025 g, almost all of the products were nanorods, while there was some tiny plate like particles, and affected the uniformity of the particles. As the concentration of SS increased to 0.15 g, HAp nanorods with diameters of ~30 nm and lengths of 500 nm - 1 μm can be obtained (Fig. 2b and b1). All of the products have nearly the same morphology and size, showing the effectiveness of this method in modifying the shape and dimensions of HAp. Further increasing SS's concentration, the length of the nanorods decreased, meanwhile, nanosphere like particles formed. Hence, compared with the other two groups, the 0.15 g group was a better choice to ensure the size and shape uniformity of HAp nanorods.

The XRD analysis was conducted, and results showed that the concentration of SS had no obvious effect on the final crystal phase of the products (Fig. 3a). Besides, according to the FTIR results, the composition among all of samples were similar, and without obvious difference can be detected, that's consistent with the XRD results.

pH value is an important factor in controlling the nucleation and determining the crystal's final morphology. Here, the relationship between pH and the shape of the products was investigated. As shown in Fig. 4, when the initial pH value was not adjusted, the products were nanorods. Increasing the pH value to 10, the final products were nanosphere like particles. Therefore, high initial pH value was not helpful for preparing rod-like particles, as it accelerated the nucleation and crystallization rate of HAp, and impaired the regulation process of SS.

In general, the self-assemble process of surfactant molecules was impacted by the concentration of ions,

Fig. 5 showed the shape and size transformation trends of HAp nanoparticles for varying Ca^{2+} concentration (C_{Ca}). For example, as C_{Ca} was 0.05 M, HAp nanoparticles with a rod-like shape with length of ~500 nm were formed. Besides, a few spherical shaped HAp particles with diameter ~ 100 nm could also be found. While at C_{Ca} = 0.15, HAp nanorod with length in the range from 400 nm to 1 μm was obtained, and the diameter was not uniform as the merging phenomenon between nanorod along the long axis. Further increasing CCa led to shorter

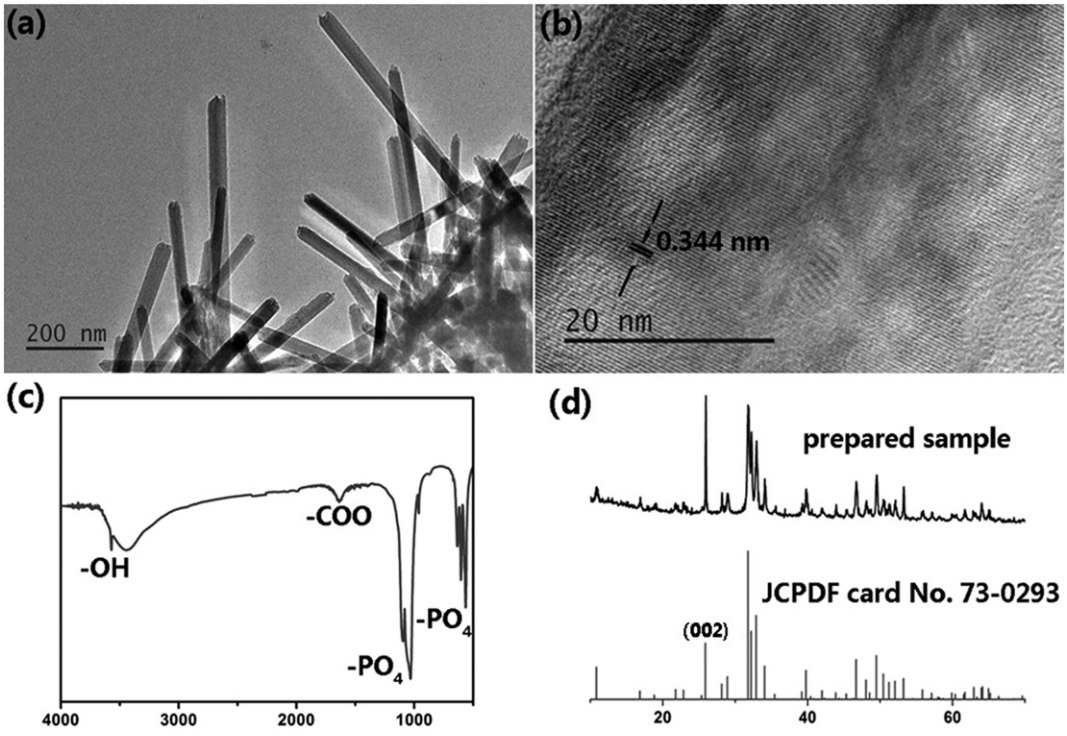

Fig. 1. The product's TEM image (a), HRTEM image (b), FT-IR (c) and XRD spectra (d). The stirring time is 5 min and concentration of SS is 0.15 g.