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Effects for rapid conversion from abalone shell to hydroxyapaptite nanosheets by ionic surfactants

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ABSTRACT

Hydroxyapatite (HAP) has been widely used for repairing or substituting human hard tissues. In this paper, two typical ionic surfactants, cation hexadecyltrimethylammonium bromide (CTAB) and anion sodium dodecyl sulfate (SDS), were used for rapid conversion of HAP from abalone shell. From field emission scanning electron microscopy (FESEM), the prepared HAP is flake-like structure. From X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal analysis, these samples contain a small amount of calcium carbonate whose content gradually increases by increasing the surfactants. The results showed that the HAP formed fast on the layer of abalone shell powder with the assistance of CTAB and SDS.

1. Introduction

Abalone is a typical kind of marine mollusk, which is a popular traditional food ingredient because of the delicious taste and high nutrition in China. Thousands of tons of abalone shell were discarded on the island and around towns after eating or processing abalone meat. As a result, natural resources are wasted and this also caused a huge burden to the environment. Abalone shell is composed of over 95 wt% calcium carbonate and 1–5 wt% of organic matter [1–3]. Thus, abalone shell is a good source of calcium. It seems that abalone shell can transform to another calcium mineral.

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has been studied extensively and applied in a variety of fields [4–7]. It is the main inorganic component of human hard tissues (such as bones, teeth, etc.) [8–11]. Owning to the excellent biological activity, biocompatibility and osteoconductivity, the synthetic nano-HAP has been widely applied to restore or substitute human hard tissues [12–15]. HAP can be synthesized by a variety of methods including solid-phase synthesis [16,17], sol-gel synthesis [18,19], template synthesis [20–22] and hydrothermal synthesis [12,23,24], etc. The hydrothermal synthesis method can make use of the original mineral that is poorly soluble or insoluble and it is easy to control the reaction conditions. Hence, the hydrothermal method has become a favorable method to prepare HAP.

Surfactants or templates are widely used to assistant and speed up the reaction for hydrothermal aqueous reaction [25,26]. The surfactants with good water-solubility, non-residual and easy wash off play an important role in nucleation and growth for aqueous hydrothermal synthesis. In the presence of extraneous additives, the surface layers of the crystal can incorporate soluble additives in the structure of the crystal boundary layers. Both the hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) are commonly used as templates because of their excellent water-solubility and non-residual [27–29]. It seems promising for rapid synthesis of HAP by hydrothermal method with the assistance of CTAB or SDS.

Herein, the abalone shell powders were used for a calcium source of HAP. HAP nanosheets were successfully synthesized with the assistance hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) via hydrothermal synthesis, where the effect of CTAB and SDS on the phase and morphology of HAP was examined. We characterized the crystal phase and morphology of the samples by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), zeta potential measurements (ZP) and a thermo gravimetric analyzer.

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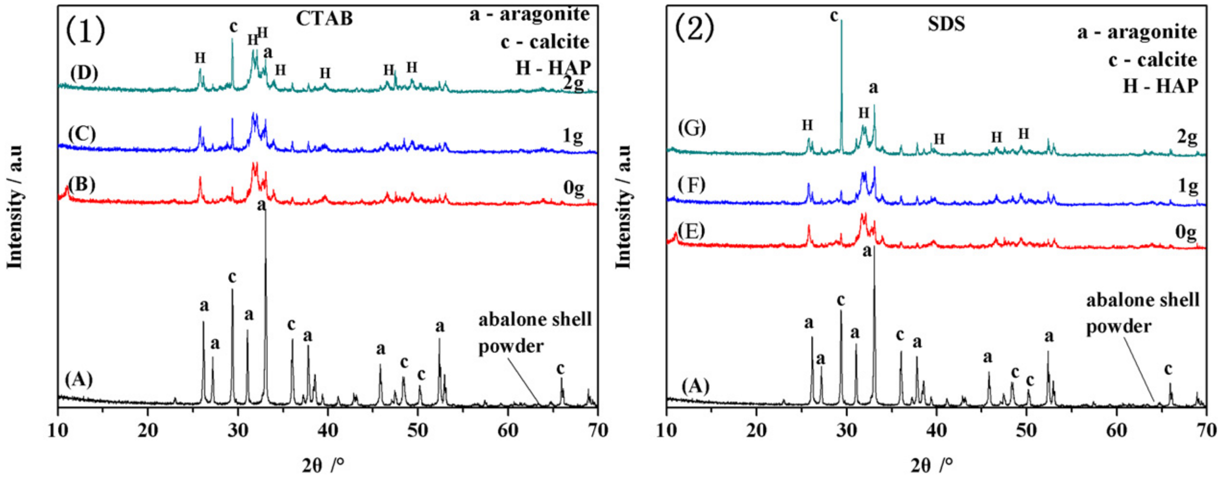

Fig. 1. XRD patterns of the samples with different surfactants.

2. Experimental section

2.1. Materials

We collected The Wrinkles abalone shells from the official dock Ocean Development Co., Ltd. (Lianjiang Country in Fujian Province, China). Diammonium phosphate ($(NH_4)_2HPO_4$, ≥99%) was bought from Sinophar Chemical Reagent Co., Ltd., China. Sodium hydroxide (NaOH, 98%) was bought from Shanghai Lianshi Chemical Co., Ltd. (Shanghai, China). Hexadecyltrimethylammonium bromide (CTAB, ≥99%) and Sodium dodecyl sulfate (SDS, ≥99%) were bought from Chinese Medicine Group Chemical Reagent Co., Ltd. (China).

2.2. Preparation of samples

First, 2 g abalone shell powders and 1.5847 g $(NH_4)_2HPO_4$ (Ca/P in a molar ratio of 1.67:1) were added in 20 ml of deionized water. Meanwhile, 2 g CTAB (or SDS) was added. The pH of solution was adjusted to 8 by sodium hydroxide solution (NaOH, 1 M) and the mixture was stirred at room temperature for 30 min using a magnetic stirrer. Then, the mixed solution was transferred into an autoclave, and heated at 90 °C with hydrothermal time for 6 h in oven. After the reaction, remove the autoclave from the oven and allow it to cool down naturally to room temperature. Finally, the collected precipitate was washed three times with distilled water and then lyophilization. After that, the samples were obtained. The control sample is prepared without surfactants.

2.3. Characterization of samples

The X-ray diffraction (XRD, X'Pert PRO Panalytical diffractometer) was used to examine the phase of the samples with Cu Kα (λ = 0.154056 nm) incident radiation at a working voltage of 40 keV in the range of 2θ from 10° to 70° at a 0.02° step size. We identified the phases by comparing the data with data in the Joint Committee of Powder Diffraction Standards database (JCPDS No. 09–0432).

For FTIR (Nicolet 360 intelligent spectrometer, Thermo Nicolet Corporation, US), a KBr pellets method was used, which was performed on dried samples.

The microstructure of the sample was studied by a hot field emission scanning electron microscopy (HFESEM, Zeiss Supra 55, Germany).

A thermogravimetric analyzer (TGA, DIL402C, NETZSCH, Germany) further measured the composition of the samples. The samples were heated to 1000 °C in flowing air at a heating rate of 10 °C/min.

The surface potential of the samples was measured by a potential instrument (Malvern Zetasizer Nano-ZS90, UK).

3. Results and discussion

XRD patterns of the samples with different surfactants are shown in Fig. 1. The diffraction peak of the abalone shell powder is showed that the abalone shell was composed of calcite and aragonite (shown in Fig. 1A). After the hydrothermal treatment, it can be observed that

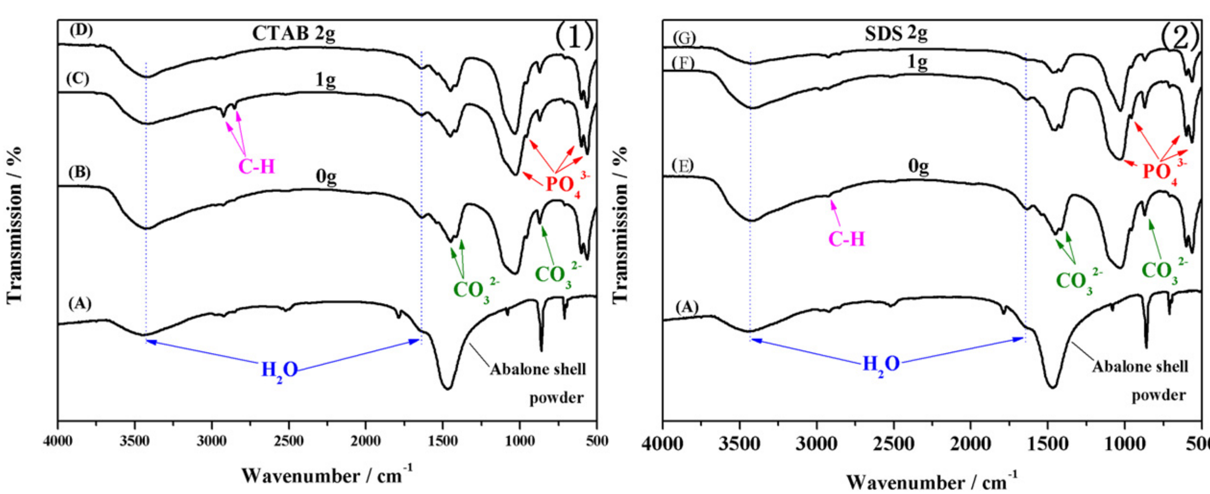

Fig. 2. FTIR spectra of the samples with different surfactants.