



Recycling of shell wastes into nanosized calcium carbonate powders with different phase compositions



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ABSTRACT

Shell wastes represent a considerable quantity of by-products in the shellfish aquaculture. From the viewpoint of eco-friendly and economical disposal, it is highly desirable to convert these residues into high value-added products for industrial applications. In this study, shell wastes from *Tapes japonica* were used to prepare nanosized calcium carbonate powders by high energy ball-milling in the sodium hypochlorite solutions. The crystal phase of powders could be changed from flake-like aragonite to spindle calcite by simply increasing the alkalinity of milling solutions, revealing the mineralizing role of strong alkaline solution. The aragonite crystallites were 20–50 nm in size, and showed porous appearance due to the presence of intracrystalline organic macromolecules. The submicron-sized calcite particles were composed of close-packed nanocrystallites, presumably deriving from the organic-induced assembly of calcite phase. The formation of different phases was ascribed to the mechanically activated exfoliation of aragonite and the dissolution–recrystallization of calcite, during which the organic matrix was decomposed by the alkaline solutions. This mechanochemical method paves the way to the industrial production of calcium carbonate powders from shell wastes and thus the clean production of shellfish processing industry.

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1. Introduction

In the past decade the marine aquaculture has been developed rapidly in the eastern and southern China. Shell wastes amounting to millions of tons were generated in the shellfish aquaculture annually, most of which were handled in the landfills. The disposal route is not only a waste of resources, but also leads to the increasingly environmental burden around the seashore. Recycling shell wastes could potentially solve the disposal issue and acquire the additional values from the shellfish processing industry, thus beneficial to the sustainable development of the marine economy (Bugallo et al., 2013).

So far, the utilization of shell wastes was confined at relatively lower levels, e.g. wastewater decontaminant, soil conditioner, fertilizer constituent, feed additive and liming agent (Kwon et al., 2009; Oliveira et al., 2013; Seco et al., 2014). Shell wastes consist of calcium carbonate and organic matrices, with the former accounting for 95–99% by weight (Furuhashi et al., 2009). Being the

richest source of biogenic CaCO₃, shell wastes are suitable to prepare high purity CaCO₃ powders, which have been extensively applied in various industrial products, such as paper, rubber, paints and pharmaceuticals (Yoo et al., 2009; Fang et al., 2014; Preisig et al., 2014). As a case in point, an eco-friendly and large-scale approach was applied to prepare high purity CaCO₃, in which the mollusk shell was calcined in the propane atmosphere to remove the organic matters (Barros et al., 2009). Islam et al. (2013a, 2013b) described a catalytic method for the synthesis of aragonite nanoparticles from cockle shells, where dodecyltrimethyl betaine was used as a biomineralization catalyst. Hydroxy-apatite powders applicable in the bone tissue engineering could also be prepared from shell wastes (Wu et al., 2011; Yang et al., 2011). Furthermore, the shell waste could be further processed to be the filler of polymer composites as well as an appropriate catalyst for biodiesel production (Li et al., 2012; Rezaei et al., 2013). These reutilizations of shell wastes shed light on the industrial production of high value-added products.

In this study, nanosized calcium carbonate powders were prepared from shell wastes by a mechanochemical method. A sodium hypochlorite aqueous solution which is the main component of ordinary disinfectant was used as the milling solution. Being an

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alkaline oxidant, sodium hypochlorite could play dual roles in the preparation process, i.e., the hydrolytic catalyst and strong oxidant of organic matters. The pH value of milling solutions was adjusted to clarify its effect on the phase composition of CaCO_3 powders, and the formation mechanism of CaCO_3 powders was qualitatively discussed.

2. Materials and methods

Raw chemicals include analytically pure sodium hydroxide and sodium hypochlorite aqueous solution with 3 wt% effective chlorine. The distilled water was prepared using an automatic aqua bi-distilling apparatus. Zirconia beads (NanorZr-93, $\varnothing 0.8$ –1.0 mm) as the milling media were purchased from Guangzhou Pleasid Grinding Media Ltd.

2.1. Preparation of CaCO_3 powders

The shell wastes were obtained from commercial freshwater shellfish (*Tapes japonica*). These wastes were washed thoroughly with household detergent, and crushed with a mortar and pestle followed by sieving through a 180 μm sieve. The coarse powder was immersed in the 5 wt% NaOH aqueous solution, and mechanically stirred at 85 $^\circ\text{C}$ for 4 h to remove the periostracum. The light yellow-colored powder was filtered, washed with distilled water, and dried overnight. The cross-section of a shell particle is characteristic of layered structure with the thickness of ~ 10 μm , as shown in Fig. 1.

Eight grams of pretreated shell powder were blended with 40 g of NaClO solution (i.e., 20 wt%) in a 50 ml polypropylene bottle, and then 80 g of zirconia beads were added. The mixed suspension was ground in a planetary ball mill (XQM, Changsha Tianchuang Technology Co.) at 400 rpm for 20 h. After that, the milled suspension was filtered, washed, and dried in a vacuum oven at 120 $^\circ\text{C}$ for 24 h. In contrast to the light-colored shell powder, snow-white CaCO_3 powders were achieved when the milling time was above 17 h. To clarify the effect of solution pH value on the phase composition, 10 and 20 weight percentages of NaOH were added into the NaClO solution respectively. The pH value of solutions was measured with a pH meter (FE20, Mettler Toledo). Finally, different milling times (1–20 h) were used to explore the formation mechanism of CaCO_3 powders.

2.2. Characterization

The crystal structure of CaCO_3 powders was analyzed by an X-ray powder diffractometer (XRD, D8 Advance, Bruker-axs) using Cu $K\alpha$ radiation. The crystal size of powders was estimated using the MDI Jade 5.0 software, and the phase composition was

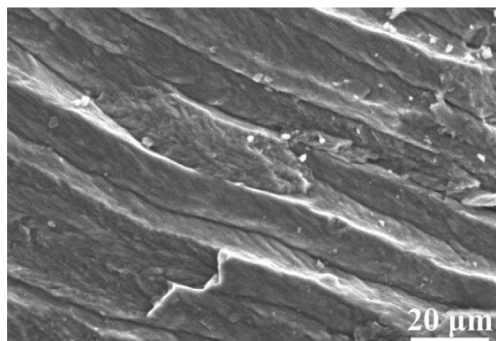


Fig. 1. SEM image of the cross-section of a shell particle.

calculated with the related RIR values of aragonite and calcite phases. The morphology of powders was studied using a transmission electron microscope (TEM, JEM-2010, JEOL). To prepare the TEM samples, dilute alcoholic suspensions of powders were ultrasonically dispersed, dropped onto carbon-coated copper grids, and dried by an infrared lamp. Chemical analysis of powders was carried out using a Fourier transform infrared spectrophotometer (FT-IR, Model 100 series, Perkin Elmer) over a range of 4000 cm^{-1} –400 cm^{-1} with a resolution of 2 cm^{-1} . The thermal behavior of powders was examined by a differential thermal/thermo-gravimetric analyzer (DTA/TGA, Pyris Diamond, Perkin Elmer) with a heating rate of 10 $^\circ\text{C}/\text{min}$ in an air flow (80 ml/min).

3. Results and discussion

Fig. 2 shows the XRD patterns of shell powder and as-prepared CaCO_3 powders. The shell powder belongs to the typical aragonite structure (PDF#71-2396) without any trace of calcite phase. However, the CaCO_3 powder prepared in the NaClO solution showed a small amount of calcite phase (PDF#83-0577). With the addition of NaOH, the calcite content was dramatically increased, and a single calcite phase was obtained ultimately with the addition of 20% NaOH.

As a control experiment, the shell powder was ground in a 10% NaOH aqueous solution for 20 h. The pH values of different milling solutions were 13.0 (NaClO solution), 13.7 (10% NaOH aqueous solution), 13.9 (10% NaOH + NaClO solution) and >14 (20% NaOH + NaClO). As shown in Table 1, the content of aragonite phase decreases monotonically with the increase of solution pH value, with the opposite result for the calcite phase. The phase transformation from aragonite to calcite implies the mineralization role of NaOH.

Various mineralizers were usually applied in the hydrothermally synthesized compounds and the biogenic materials of shellfishes (Nudelman and Sommerdijk, 2012; Einarsrud and Grande, 2014). The addition of alkaline hydroxides (e.g. NaOH, KOH and LiOH) increases the ionic strength of solutions, facilitating the dissolution–recrystallization process (Byrappa and Ohachi, 2003). Thus, the complete transformation of aragonite to calcite could be explained by means of the mineralizing role of NaOH solutions. Similarly, the high alkalinity of NaClO solution contributed to the trace amount of calcite phase. Moreover, it should be pointed out that the calcite phase existing in the prismatic layer of shell

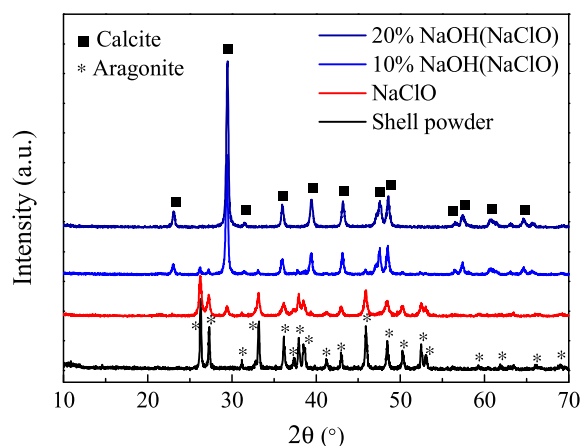


Fig. 2. XRD patterns of shell powder and CaCO_3 powders from different milling solutions.

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