One-step hydrothermal transformation of oyster shell Mg-calcite to biomimetic nanocrystalline apatite

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Seashells are hierarchical bio-organic/mineral composites made of calcium carbonate ($CaCO_3$) and an organic matrix (1-5 wt. %) composed mainly of proteins and polysaccharides. Fishery industry waste containing seashells from mussels, scallops, and oysters, represents an important environmental issue. The process is ecologically harmful and implies the loss of potentially useful biomaterials [1]. The valorization of seashell waste by transforming the $CaCO_3$ crystals into biomimetic apatite micro/nanoparticles for biomedical applications may have a positive environmental impact besides economic profitability since the global market (including nano-sized, micron-sized, and higher sizes) is expected to grow in the next years. Different methods to transform biogenic $CaCO_3$ into apatite nano/microparticles have been developed recently. They are mainly two-step processes involving calcination to CaO at 900-1000 °C followed by the reaction of a phosphate reagent (typically H_3PO_4) with the $Ca(OH)_2$ produced by hydration of the CaO [2]. In this work, we have developed a one-step hydrothermal process to obtain biomimetic carbonated-apatite using oyster shells (Mg-calcite, 5 wt.% Mg) from the species *Crassostrea gigas* as model raw material. Shells were treated with NaClO 5% v/v to remove surface organic residues, crushed by a hammer mill, milled in a ball mill and sieved using a <45 μm mesh. The so obtained particles were submitted to hydrothermal treatment. Different experimental parameters were tested: P reagents (H_3PO_4, KH_2PO_4, and K_2HPO_4); P/Ca molar ratios (0.24, 0.6, and 0.96); temperature (25-200°C) and time (from 1 week to 2 months), without any pH adjustment. Characterization was performed by XRD, FTIR, Raman, SEM, TEM, DLS and TGA. The apatite/calcite ratio (wt.%) of the final precipitates was determined by Rietveld analysis using TOPAS 6.0 software. Among the many results, it is worth of mentioning that at the lowest experimental time used (1 week), the temperatures to obtain full transformation depend on the P reagent and P/Ca mol ratio, the lowest one being 80 ºC when using KH_2PO_4 as reagent, and a P/Ca molar ratio 0.96 (excess of P). The obtained precipitates (Mg^{2+}-doped carbonated-apatite micro/nanoparticles) with biomimetic features are the result of a dissolution/reprecipitation mechanism driven by pH variation. Compared to the previous two-step processes, the one reported here is straightforward, one-pot, and can be operated at relatively low temperatures without any pH adjustment, and specially avoiding the use of expensive hydrothermal autoclaves.

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