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A novel catalytic method for the synthesis of spherical aragonite nanoparticles from cockle shells

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A B S T R A C T

For the first time, we report here a novel top down catalytic approach for the synthesis of aragonite nanoparticles with spherical morphology from cockleshells. Cockle shell is a natural reservoir of aragonite which is a biogenic polymorph of calcium carbonate. Aragonite polymorph is widely used in the repair of fractured bone, development of advanced drug delivery systems, and tissue scaffolds. The method involves an easily performable and low-cost mechanical stirring of the micron-sized cockle shell powders in presence of a nontoxic biomineralization catalyst, dodecyl dimethyl betaine (BS-12). It produces spherical shaped aragonite nanoparticles of 35 ± 5 nm in diameter with a good reproducibility and without any additional impurities at room temperature. The findings were verified with a variable pressure scanning electron microscopy (VPSEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM),Fourier transmission infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), and thermogravimetric analyzer (TGA).The reproducibility, low-cost and simplicity of the method suggested its potential applications in large scale synthesis of aragonite nanoparticles with spherical morphology in an industrial set up.

1. Introduction

Synthesis of nanoparticles with desired sizes, shapes and morphologies has wide ranging interests in industry, biomedical and optoelectronic devices, sensor technologies as well as agriculture, environment and food industry [1]. At present, nano-hydroxyapatite is used in bone paste [2], and calcium carbonate ($CaCO_3$) nanoparticles are used in the preparation of acrylic bone cement *in vitro* [3].Being a cheap and commercially available inorganic particle, $CaCO_3$has been extensively used in many industrial products, such as paints, inks, papers, plasticisers, feed-stuff, medicine and biomaterials [4].$CaCO_3$can exist in three polymorphic forms: calcite, vaterite and aragonite [5]. Aragonite is biocompatible, denser than calcite and can be integrated, resolved and replaced by bone [6]. In addition to regular uses [3,4], aragonite nanoparticles (ANP) can be used to develop advanced drug delivery systems and scaffolds for bone repair and tissue engineering [6]. Cockle shell is a natural reservoir of purified aragonite and recently, we have documented a novel method for the synthesis of rod-shaped aragonite nanoparticles from this low-cost and abundant natural resource [6]. However, it has been widely reported that the properties of nanomaterials and nanoparticles are size, shape and morphology dependent [7]. For examples, honey comb gold nanoflakes have superior optoelectronic properties than ordinary gold flakes. Therefore, there is an increasing demand for methodologies for the synthesis of nanoparticles with various morphologies, sizes and shapes to streamline their applications in specialized areas.

Spherical mineral nanoparticles behave quite differently from layered silicates and fibres [8]. The low aspect ratio and large surface area of spherical inorganic nanoparticles result in strong interfacial interactions between the filler and the polymermatrices [9] and provide them superior dispersion properties in various solvents [9]. Nanoscale$CaCO_3$is one of the most common spherical nanoscale fillers used in the preparation of nanocomposites and cementing materials for various uses [10]. Currently, various template aided methods such as Langmuir monolayers, self-assembled monolayers, functionalized polymer surfaces, lipid bilayer stacks, crystallization inhibitors, microemulsions, agarose gel and aqueous foam film lamellae are being used for the size- and shape-controlled synthesis of $CaCO_3$

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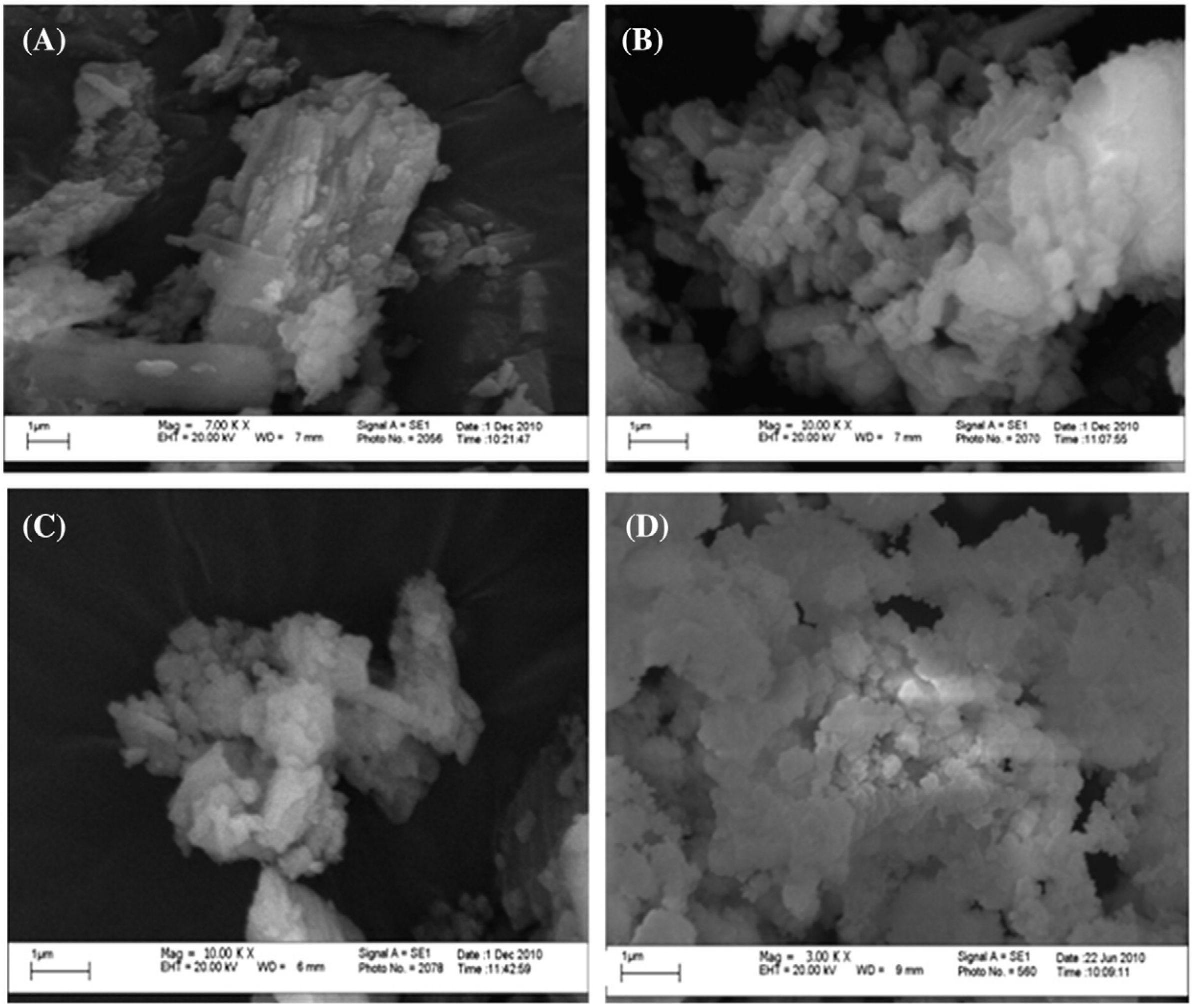

Fig. 1. SEM micrograph of (A) cockle shell powders in the absence and (B) in the presence of BS- 12 with 110 (B); 120 (C); and 130 min (D) of constant stirring. Large,rod-shaped aragonite crystals were observed in the absence of BS-12(A), whereas aggregated clumps of spherical particles appeared in presence of BS-12(B-D). The degrees of agglomeration were increased with BS-12 incubation time.

nanoparticles [10]. However, these methods need purified and expensive chemicals, sophisticated instrumentations, expertise skills, multiple steps and extensive preparation time and thus they are not suitable for large-scale industrial synthesis. Additionally, most of the time, they added impurities and come up with mixtures of various polymorphs which may not be suitable for specialized applications. Here we documented a catalytic method that takes only 2 h, need only very simple instrumentations and general skills to synthesize purified and spherical aragonite nanoparticles from a low-cost and abundant natural resource, cockle shell, at room temperature. It is only a mechanical grinding in the presence of a non-hazardous biomineralization catalyst, BS-12.

2. Experimental

2.1. Preparation of micron-sized cockle shell powders

The micron-sized cockle shell powders were prepared according to our previous report [5]. Briefly, 250 gm of cockle shells (*Anadaragranosa*) were washed, scrubbed to remove dirt, boiled for 10 min and then cooled at room temperature. The shells were then washed thoroughly with distilled water and dried in an oven (Memmert UM500, Germany) for seven days at 50 °C. The cockle shells were finely grounded using a blender (Blendor, HCB 550, USA). The powders were sieved using a stainless laboratory test sieve with an aperture size of 90 μm (Endecott Ltd., London, England) to obtain micron-sized (10–90 μm in diameter) powders [5].The water used was HPLC-grade of resistance > 18MΩ obtainedfrom a Milli-RO6 plus Milli-Q-Water System (Organex).

2.2. Preparation of nano-sized cockle shell powders

Five grams of micron sized cockle shell powders were taken into a 250 ml conical flask.A slurry was formed by adding and mixing 50 ml of distilled water. The conical flask was shacked in an oil bath shaker for 24 h at 80 °C. To synthesize $CaCO_3$ nanoparticles, 1 ml of BS-12 (as obtained from Sigma Aldrich, Steinheim, Germany) was added into the conical flask and was vigorously stirred at 1000 rpm at room temperature for 110 min, 120 min and 130 min using a Systematic Multi-Hotplate and magnetic stirrerbar. The control was treated with equivalent volume of distilled water for 120 min. The prepared sample was separated from the mother liquid using a double ring filter paper of size 18.0 cm (FiltresFioroni, China). The final products were dried for 2 day in an oven (Memmert UM500, GmbH Co, Germany) at 80 °C and packed in a polyethylene plastic bag (JP Packaging) for further uses.