Materials Letters 160 (2015) 167–170

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Preparation of mesoporous calcite with hierarchical architectures

Sheng-Hui Yu [a], Han Li [a], Qi-Zhi Yao [b], Gen-Tao Zhou [a,*], Sheng-Quan Fu [c]

[a] CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China
[b] School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China
[c] Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, PR China

ARTICLE INFO

Article history:
Received 12 June 2015
Received in revised form
18 July 2015
Accepted 21 July 2015
Available online 23 July 2015

Keywords:
Calcite
Porous materials
Morphology
Microstructure

ABSTRACT

Mesoporous calcite with different architectures is successfully prepared via a facile microwave-assisted polyol process, followed by a calcination treatment. The precursor, obtained by microwave-assisted method in EG solvent without any other organic additives, is a composite of aragonite–calcium acetate hydrate. The morphology and contexture of the precursor could be easily adjusted by the different addition of urea. After calcination, the as-synthesized precursor can be transformed into pure calcite with intact morphology and architecture. The BET surface area and total pore volume are 22.70 m^2/g and 0.044 cm^3/g for the flower-like calcite, and 39.97 m^2/g and 0.115 cm^3/g for the hierarchically layered calcite, respectively.

1. Introduction

The synthesis of inorganic materials with well-defined architectures based on the construction of nanounits (nanowires, nanosheets, nanoneedles, nanobelts or nanotubes) has gained considerable attention over the past years, owing to their importance in basic scientific research and potential technological applications [1,2]. Calcium carbonate is an important mineral material due to its significance as a biomineral and to widely industrial applications for plastics, rubbers, papermaking, biomedical implant, drug delivery, and water treatment [3–7]. It exists in three anhydrous crystalline polymorphs: rhombohedral calcite, orthorhombic aragonite, and hexagonal vaterite. Of them, calcite is thermodynamically the most stable one, followed by aragonite and then vaterite. The common morphologies of the $CaCO_3$ polymorphs are rhombohedral calcite, needle or rod-like aragonite, and spherical vaterite [4]. The application of $CaCO_3$ is decided by a number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, chemical purity and so on, which depends on the methods of preparation [8]. Moreover, the control of $CaCO_3$ morphology has been an important subject in biomineralization and biomimetic mineralization [9,10]. Therefore, the fabrication of $CaCO_3$ crystals with complex structures has received much attention. The biomimetic method is a common way to prepare $CaCO_3$ with specific morphologies and hierarchically organized structures. For example, vaterite mesocrystals with a hexagonal prism structure were achieved by the use of sodium citrate and sodium dodecyl benzenesulfonate [11]. Aragonite nanorod aggregates with unusual morphologies were prepared with the help of natural fibrous proteins [12]. Calcite with thin films and abundant nanofibers was produced in the presence of poly(aspartic acid) and magnesium ions [13]. Nacre-like aragonite/poly (acrylic acid) multilayer film was fabricated on a natural nacre substrate [14]. Other reported methods to obtain $CaCO_3$ with well-defined architectures include the additive-mediated method [8], surfactant-assisted approach [15], and template-assisted method [16]. Herein, we report the synthesis of mesoporous calcite with hierarchical architectures via a microwave-assisted polyol process, followed by a calcination treatment. To the best of our knowledge, no similar architecture mesoporous calcite has been reported so far.

2. Experimental

All chemicals were analytical grade reagents and used as received without further purification. In a typical synthetic process, 2 mmol of calcium acetate monohydrate ($Ca(CH_3COO)_2 \cdot H_2O$) and 2 mmol of urea ($CO(NH_2)_2$) were successively dissolved in 20 mL of ethylene glycol (EG) in a 100 mL round-bottomed flask by ultrasonication. Then the round-bottomed flask with the reactants was equipped on a microwave reactor (WBFY-201, Yuhua, Gongyi,

---

[*] Corresponding author. Fax: +86 551 63600533.
E-mail address: gtzhou@ustc.edu.cn (G.-T. Zhou).

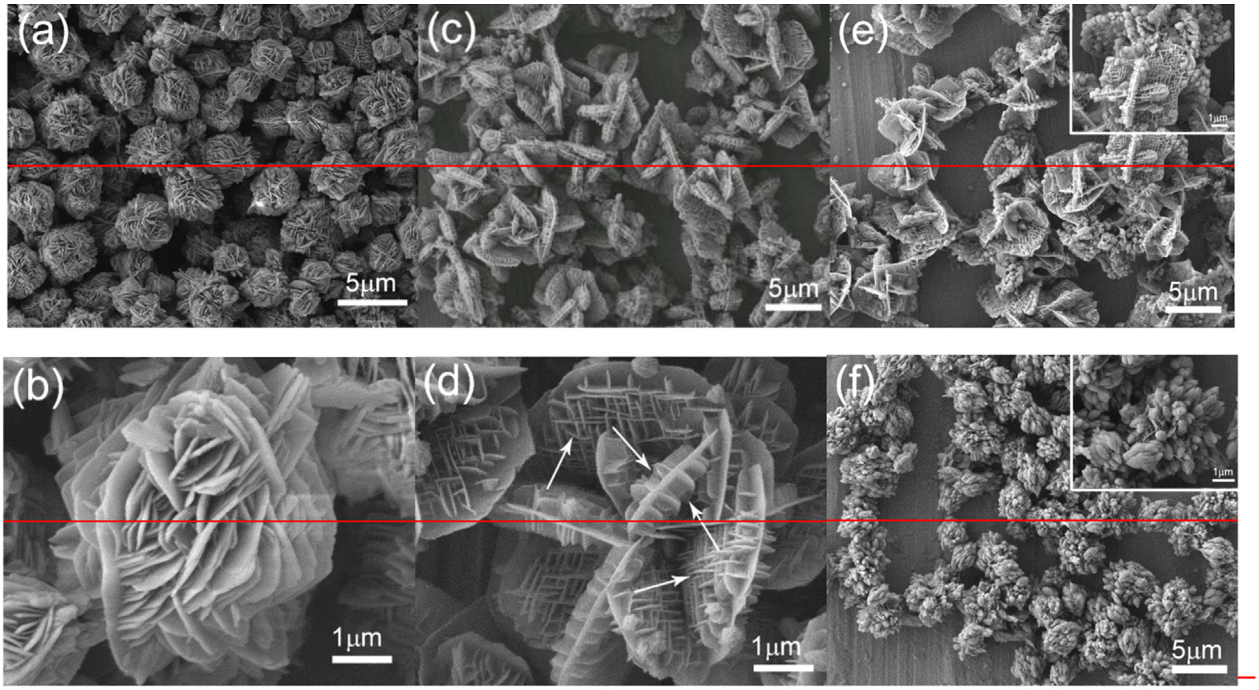
http://dx.doi.org/10.1016/j.matlet.2015.07.116
0167-577X/© 2015 Elsevier B.V. All rights reserved.

China), and irradiated for 10 min at 50% of the full power to produce a white precipitate. The white precursor was collected by centrifugation and washed with ethanol three times, and then dried in a vacuum oven overnight at 40 °C. The dried white precursor was calcined at 500 °C for 2 h in air by a programmed furnace (KSL-1100, Kmt, China) to obtain the final product. After cooling to room temperature, the calcined product was collected for further characterizations.

Several analytical techniques were used to characterize the precursor and the final product. Powder X-ray diffraction (XRD) patterns were recorded with a Japan Map XHF X-ray diffractometer. Morphology and microstructures were observed by JEOL JSM-2010 field-emission scanning electron microscopy (FES-EM). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the precursor were carried out on SDT Q600 thermal analyzer with a heating rate of 10 °C min^{-1} in air. N_2-sorption isotherms of the final products were measured using a Micromeritics Tristar II 3020 Minstrument at liquid-nitrogen temperature.

3. Results and discussion

Fig. 1 shows the SEM images of precursors prepared with



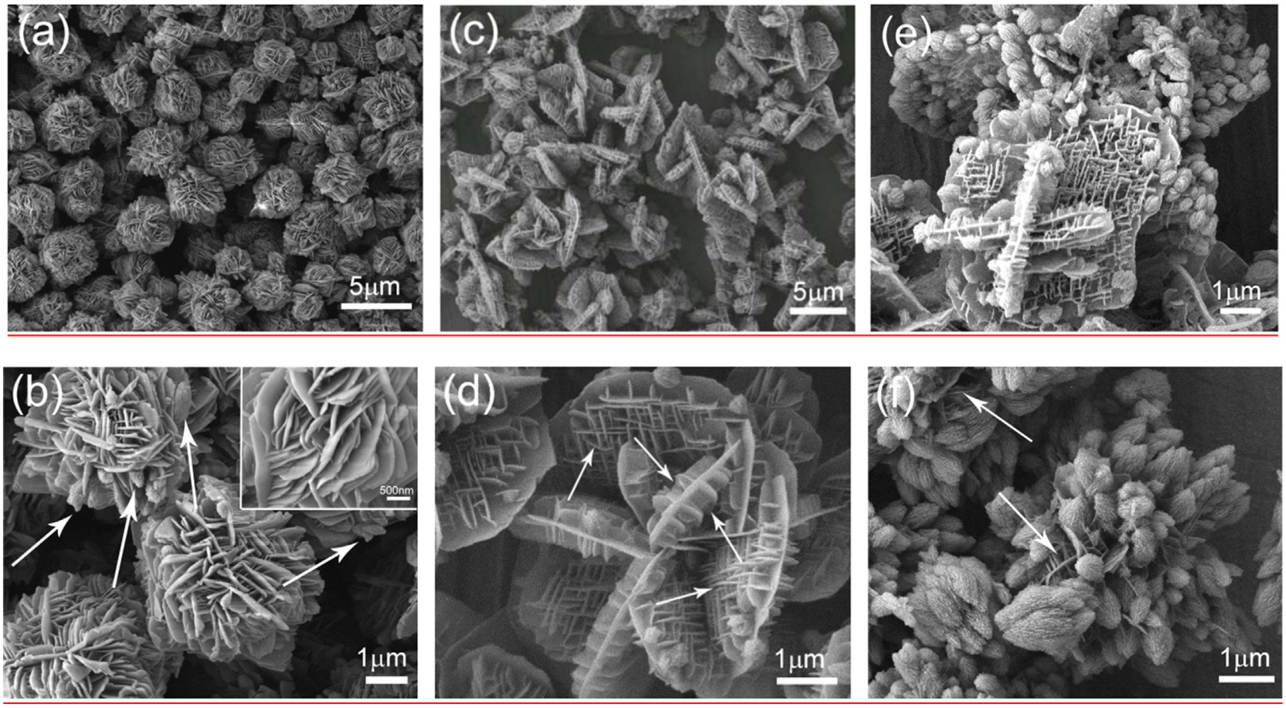


Fig. 1. SEM images of precursors obtained with different amounts of urea: 2 (a, b), 6 (c, d), 10 (e) and 14 mmol (f).