Materials Letters xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Materials Letters

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

Hierarchical pine-dendritic vaterite preparation and micropatterning with microwave technique

Xiaohong Wang [a], Xinyuan Sun [a], Qun Zhang [a], Alessandro Marchetti [b], Lin Wu [a], Yebin Guan [a,b,*]

[a] Anhui Key Laboratory of Functional Coordination Compounds, School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, PR China
[b] Center for Chemistry of Novel & High-Performance Materials, and Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 12 March 2017
Received in revised form 10 May 2017
Accepted 11 May 2017
Available online xxxx

Keywords:
Crystal structure
Crystal growth
Vaterite
Microwave

ABSTRACT

The preparation of pine-dendritic vaterite with microwave-assisted technique in ethylene glycol (EG)/water solution was investigated. The samples were characterized with a broad range of techniques, including FESEM, XRD, TGA and HRTEM. Results show that the combination of microwave radiation and EG/water solution conduced to the formation of pine-dendritic crystals with the assembling of vaterite sheets. The inhibition of EG molecules on the {00.1} faces of vaterite contributed to the formation of vaterite sheets, and mutually electrostatic attraction of vaterite polar {00.1} faces promoted the assembly of vaterite sheets into pine-dendritic microcrystals. This study can serve as a successful paradigm for fabrication of hierarchical structure materials.

1. Introduction

$CaCO_3$ can crystallize in various hierarchical architectures as calcite, aragonite and vaterite, with numerous potential applications [1–4]. Among them, vaterite shows unique properties such as high solubility, high dispersion, high specific surface area, and lower specific gravity [5–7]. However, developing simple synthetic approaches for $CaCO_3$ specific polymorphs is still challenging. Compared with some conventional methods such as hydrothermal, solvothermal, sol-gel, etc., microwave (MW) synthesis has been accepted as a promising technology for many composites with different scales [8,9], because of its short reaction time, small particle size and more pure and highly crystalline products with narrow size distribution by adjusting the reaction conditions [10,11]. Furthermore, MW method is important in providing scaled-up processes without thermal gradient effects [12,13]. Nonetheless, the preparation of $CaCO_3$ with hierarchical structure via MW method has not been addressed in the scientific literature to date [14].

In this paper, we successfully prepared vaterite in an EG/water solution via MW technique. FESEM images showed that vaterite crystals with higher-order superstructures were formed through the assembly of thin vaterite sheets. The surface charge of these sheets was pinpointed as the significant driving force for the formation of the superstructures.

2. Results and discussion

Fig. 1 shows the typical FESEM images of the products prepared from the EG/water solutions and Fig. 2 the relative XRD patterns. Without EG, the panoramic image (Fig. 1a) and the XRD pattern (Fig. 2a) indicated that the vast majority of crystals expressed calcite characteristic rhombohedron, while a small quantity of rod-like aragonite crystals also appeared [15]. With 40% volume ratio of EG, the largest amount of crystals were calcite rhombohedra, accompanying a small amount of sheet-like aggregates (Fig. 1b). XRD pattern demonstrated that the majority of the product was calcite, containing a small amount of vaterite and aragonite (Fig. 2b). With the volume ratio of EG being increased to 60%, the greater part of product showed fasciculate morphology in associated with a small amount of calcite rhombohedra (Fig. 1c). Fig. 2c demonstrated that the dominating form was vaterite, together with a small amount of calcite and aragonite, therefore crystals with fasciculate morphologies in Fig. 1c could be identified as vaterite. With EG further being increased to 80%, Fig. 1d revealed that the pine-dendritic morphology, which can be taken for that sheet-like microcrystals assembled orderly in a certain orientation. XRD pattern (Fig. 2d) revealed that the vast amount of product is vaterite, with a minute quantity of calcite and aragonite.

When EG volume ratio was further increased to 92%, almost all the crystals express the pine-dendritic morphology with thin

* Corresponding author at: Anhui Key Laboratory of Functional Coordination Compounds, School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, PR China.
E-mail address: guanyb@aqnu.edu.cn (Y. Guan).

http://dx.doi.org/10.1016/j.matlet.2017.05.057
0167-577X/

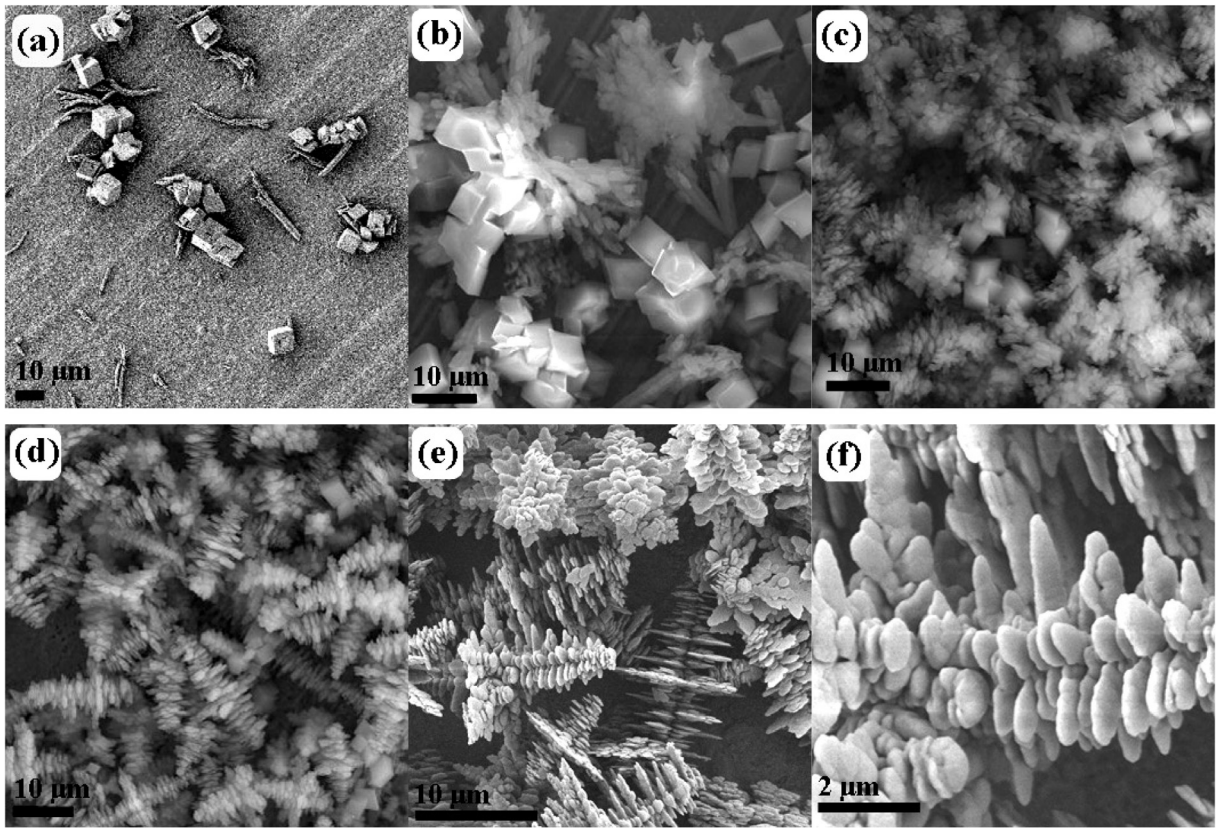

Fig. 1. FESEM images of the simples obtained in EG/water mixed solvent systems. The volume ratio of EG was: (a) 0%, (b) 40%, (c) 60%, (d) 80% and (e, f) 92%.

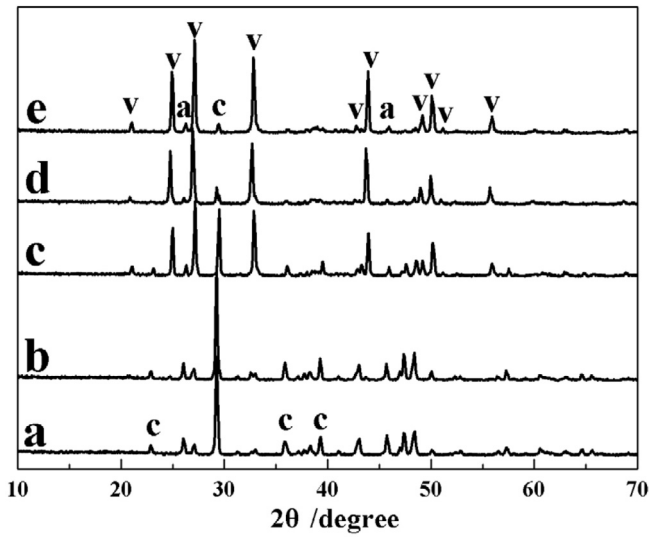

Fig. 2. XRD patterns of the samples obtained from EG/water solutions. The volume ratio of EG was: (a) 0% (b) 40%, (c) 60%, (d) 80% and (e) 92%. The letters c, v and a indicate calcite, vaterite and aragonite, respectively.

sheet-like microcrystals assembly (Fig. 1e), the amplified image (Fig. 1f) clearly revealed that ca. 200 nm thin sheets orderly assembled with homogenous orientation with a plane-to-plane fashion. Interestingly, these sheets engaged with each other with extremities revolving around a center and other sections staggered to form the special pine-dendritic morphology. Fig. 2e demonstrates that the sample was mostly vaterite with a minute quantity of calcite and aragonite. This suggests that the pine-dendritic assembled crystals were vaterite.

Fig. 3a shows the TEM image of a thin sheet which stripped from dendritic vaterite (Fig. 1e) after 30 min ultraphonic treatment. Fig. 3b is the amplified TEM image of the box area indexed in Fig. 3a. This thin sheet is clearly composed of nanoparticles with sizes of 25–50 nm. The SAED pattern (Fig. 3c), which was taken from the single hexagonal vaterite sheet in the box area in Fig. 3b, can be indexed as a hexagonal vaterite single crystal (hexagonal space group P_{63}/mmc) viewed from the [001] zone axis. The appearance of periodic diffraction spots indicated that these seemingly randomly arranged particles in Fig. 3b self-assembled into highly oriented aggregates, and diffracted as a single crystal. The SAED result demonstrated that the crystallographic axes of all the nanoparticles in the thin crystallized sheet are parallel. Each vaterite sheet can be considered to consist of aggregates of nanoparticles that share the same 3-dimension orientation. HRTEM images (Fig. 3d and e) of this sheet with a clearly resolved lattice fringe of the (100) planes (d = 0.3558 nm) further confirmed the single-crystalline nature of each vaterite plate. Moreover, from Fig. 3e it can be clearly seen that vaterite nanoparticles have the same orientation but are separated by some amorphous nanoparticles (as shown in Fig. 3e by white arrows), indicating that these vaterite sheets actually have mesocrystal structures [16], with the typical preferential orientation of their aggregated nanoscale subunits. Herein, it is remarkable that nanoparticles can give rise to oriented aggregation to form thin aggregated sheets.

A TGA measurement was conducted on the product obtained from the EG volume ratio of 92% reaction. Fig. 4 showed that a first step of decomposition starts at ca. 250 °C and ends at ca. 555 °C with a weight loss during this stage of about 3.1%. Such data could be associated to the decomposition of the EG molecules, which means that EG molecules are chemically adsorbed on the surface of the $CaCO_3$ crystals after washing-up with alcohol and distilled

Please cite this article in press as: X. Wang et al., Hierarchical pine-dendritic vaterite preparation and micropatterning with microwave technique, Materials Letters (2017), http://dx.doi.org/10.1016/j.matlet.2017.05.057