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Using Simple Hydrothermal Method for Synthesis of $CaCO_3$ Plate-like Nanostructures

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$CaCO_3$ nanostructures were synthesized via hydrothermal method by $Ca(NO_3)_2.4H_2O$, ethylenediamine (en) and hydrazine as precursors. Different parameter effects were investigated on product size and morphology. The product was characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDAX), Fourier transform infrared spectroscopy (FT-IR) and room temperature photoluminescence spectroscopy (PL).

Keywords: $CaCO_3$, Hydrothermal, Nanostructures.

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1. INTRODUCTION

Calcium carbonate ($CaCO_3$) is one of the most abundant minerals in nature [1]. The industrial applications of $CaCO_3$ are wide ranging, including paper, paints, inks, plastics, medicines, feedstuff, adhesives and rubbers [2]. $CaCO_3$ has three polymorphs of stable calcite, metastable aragonite and unstable vaterite, which have the crystal system of rhombohedral, orthorhombic and hexagonal, respectively. The thermodynamic stability of the three polymorphs at atmospheric temperature and pressure is in the order calcite > aragonite > vaterite. Because the morphology and physicochemical properties such as solubility and density depend on each polymorph, the polymorph control of $CaCO_3$ crystals is very important in a crystallization process [3]. Many approaches have been developed to control the phases and the morphologies of $CaCO_3$ in order to meet the demands in practical applications. The former methods mainly focused on the study of organic additives on the crystallization of calcium carbonate, such as the formation of sponge-like vaterite in the presence of sodium dodecylsulfate [4], the deposition of calcium carbonate thin films on decalcified eggshell membrane and Nylon 66 Knits with acidic polymers as polyaspartic acid and polyglutamic acid [5], the solvothermal growth of vaterite in the presence of glycol, 1,2-propanediol and glycerin [6] and the crystallization of needle-like vaterite calcium carbonate using the cooperative effect between Mg^{2+} and the gold nanoparticles [7]. Hydrothermal synthesis has been regarded as one of most effective and economical routes, as it has the merits of one-step low-temperature synthesis, powder reactivity, and shape control [8]. In this work, we synthesized $CaCO_3$ nanostructure via simple hydrothermal methods. The effect of reaction temperature was investigated on product size and morphology.

2. SYNTHESIS AND CHARACTERIZATION

2.1 Method of Sample Manufacturing and Analysis

In a typical experimental method, 1 g of $Ca(NO_3)_2.4H_2O$ was solved in 50 ml distilled water and then ethylenediamine with 1 : 4 mole ratio in comparison to calcium source was added dropwisely to above solution with vigorous stirring. After stirring the solution for 30 min, 0.42 ml hydrazine was dissolved in 50 ml distilled water and added to reaction medium. Finally the reagents were transferred to autoclave with 500 ml capacity. Autoclave was placed at the oven and the reaction was done at 140-180 °C for 24 hours and cooled gradually in room temperature. Obtained precipitate was centrifuged and washed several times with distilled water and absolute ethanol for removing probably by products and then dried at 80 °C for 10 h and were characterized by SEM, PL, EDS, and XRD analyses.

3. RESULT AND DISCUSSION

Fig. 1 shows room temperature photoluminescence of sample No. 14. Calculated band gap for this product was 3.27 eV that has 0.39 eV blue shift in comparison to bulk $CaCO_3$ with aragonite structure (2.88 eV) [9]. This is due to smaller particle size of the sample compared with the bulk one.

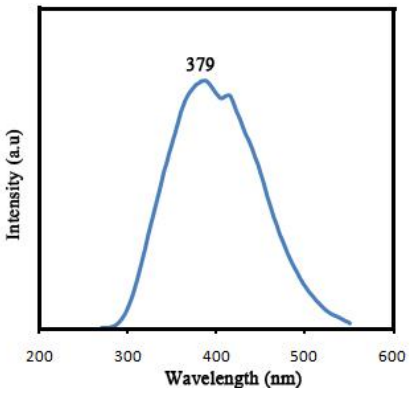

Fig. 1 – PL spectra of $CaCO_3$ nanostructure prepared at 160 °C for 24 h

Fig. 2 shows the effect of hydrothermal temperature on product size and morphology. When the reaction temperature was selected to 140 °C, the product was com-

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posed from angular and irregular micro spheres (Fig. 2a). When the reaction temperature was increased to 150 °C, the spheres became regular and cubic-like structures were obtained (Fig. 2b). By increasing the reaction temperature to 160 °C, the product is composed from two groups of nanoplates that are perpendicular to each other (Fig. 2c). These groups make cubic structures jointly. With the progress of reaction at 170 °C for 24 h, the nanoplates make cubic-like structures again (Fig. 2d). Finally using 180 °C temperature for synthesizing of $CaCO_3$ nanostructures was led to creation of large plates and accumulated particles (Fig. 2e).

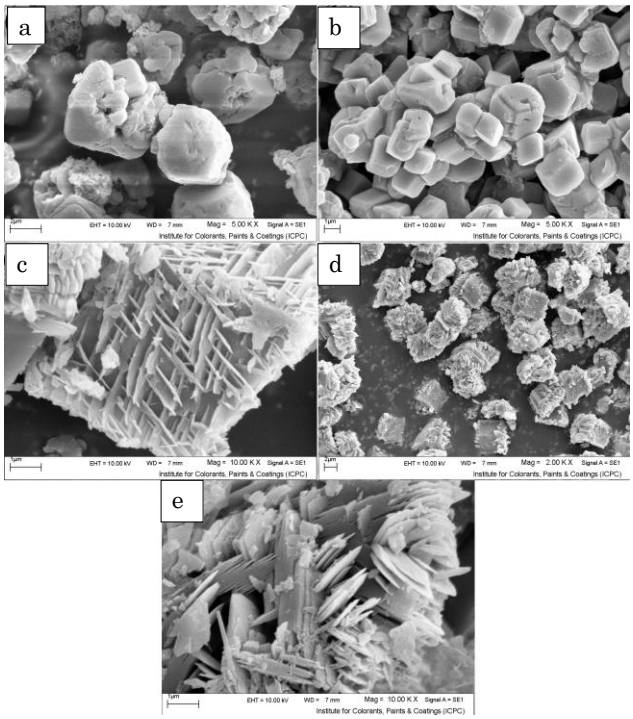

Fig. 2(a-e) – SEM image of $CaCO_3$ nanostructures at 140-180 °C for 24 h, respectively

Fig. 3 shows XRD pattern of $CaCO_3$ prepared in 160 °C for 24 h. The product is composed from Rhombohedral (JCPDS No. 86-2339) and orthorhombic (JCPDSNo. 03-0893) phases. Calculated crystal size for this sample from deby-sherrer equation was about 46.33 nm. The chemical purity was examined with Energy dispersive Analysis X-Ray (EDAX) spectroscopy. As it shown in Fig. 4 there are strong peaks related to calcium, oxygen and carbon. Therefore $CaCO_3$ with high purity was synthesized. Si peak is related to use siliceous substrate for analysis.

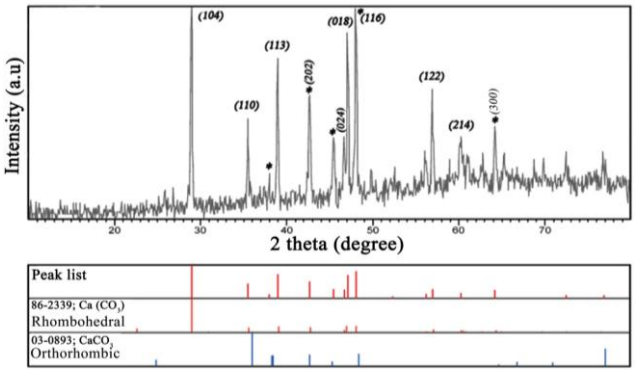

Fig. 3 – XRD pattern of $CaCO_3$ nanostructure prepared at 160 °C for 24 h

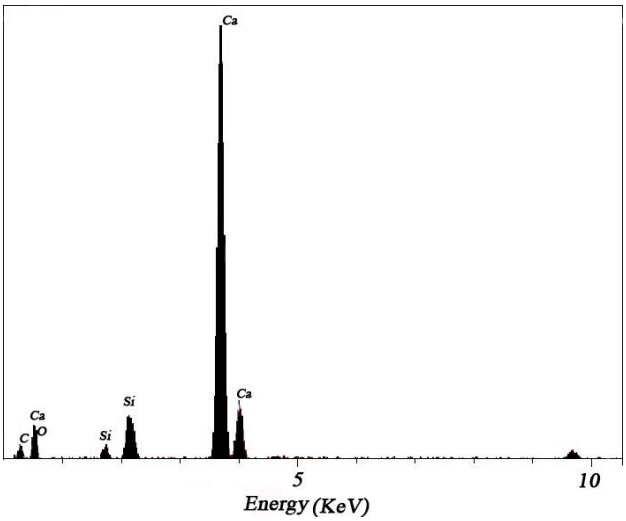

Fig. 4 – EDAX spectra of $CaCO_3$ nanostructure prepared at 160 °C for 24 h

4. CONCLUSION

In this work $CaCO_3$ plate-like nanostructures were synthesized successfully via simple microwave approach. The effect of reaction temperature was investigated on product size and morphology. It was found that by increasing hydrothermal temperature the morphology of products tend to plate-like nanostructures.

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