STUDY ON SYNTHESIS OF $CaCO_3$ NANOPARTICLES FROM CaO AND Na_2CO_3 PRECURSORS BY PRECIPITATION METHOD

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TÓM TẮT

NGHIÊN CỨU TỔNG HỢP NANO $CaCO_3$ TỪ TIỀN CHẤT CaO VÀ Na_2CO_3 BẰNG PHƯƠNG PHÁP KẾT TỦA

Nano $CaCO_3$ là một vật liệu quan trọng nhờ vào tính tương thích sinh học, độ ổn định hoá học cao, phù hợp trong nhiều ứng dụng trong y học, dược phẩm, xử lý môi trường và một số ngành công nghiệp khác. Nghiên cứu này mô tả quá trình tổng hợp nano $CaCO_3$ bằng phương pháp kết tủa với các tiền chất ban đầu CaO và Na_2CO_3. Quá trình tổng hợp $CaCO_3$ được tối ưu hoá dựa trên điều khiển các yếu tố ảnh hưởng (thời gian khuấy, tốc độ khuấy của bình phản ứng) tới quá trình tổng hợp dung dịch $Ca(OH)_2$ trung gian để đạt hàm lượng tối ưu, độ sạch cao. Nano $CaCO_3$ thu được sau đó được đánh giá bằng các kỹ thuật hoá lý hiện đại như phân tích nhiệt (DTA/DSC), phương pháp phân tán năng lượng bề mặt (EDS), kính hiển điện tử quét (SEM) và truyền qua (TEM), phương pháp nhiễu xạ tia X (XRD) và hồng ngoại (FTIR). Sản phẩm nano $CaCO_3$ thu được có độ sạch cao, kích thước ≤ 200nm dạng tựa khối lập phương. Quy trình được đưa ra có hiệu quả tốt và có khả năng ứng dụng trong thực tế.

Từ khoá: *nano $CaCO_3$, kết tủa, tổng hợp có điều khiển.*

1. INTRODUCTION

$CaCO_3$ nanoparticles (NPs) were known as an important material for applications in medicine, pharmaceuticals, industries, and others. The common applications are drug delivery, calcium supplements, the manufacture of composite materials, environmental treatments, and so on[1-4]. $CaCO_3$ NPs became a high priority in many aspects due to their highly biological compatibility, good chemical stability, and highly specific surface area[5,6]. $CaCO_3$ NPs were typically prepared by precipitation, carbonatization, or sol-gel methods. The precipitation method provided the advantages of simplicity, cost-effectiveness, and controllable-size particles, but required a strict quality control of raw materials for production[7,8]. Carbonatization offered a direct synthesis of $CaCO_3$ NPs via the blow of a CO_2 stream into Ca^{2+} ($Ca(OH)_2$) solution[9], whereas the sol-gel method generated the particles with highly uniform size and purity[10,11]. However, both methods required a high cost with the complicated equipment and procedures. In this study, the authors employed the simple precipitation method and attempted to optimize several synthesis conditions, mainly to control the step of $Ca(OH)_2$ solution preparation, to obtain the desirable particle size with high purity and stability for specific purposes in medicine and industry. Calcium oxide (CaO) and sodium carbonate (Na_2CO_3) were used as the precursors for Ca^{2+} and CO_3^{2-} for this synthetic procedure to ensure the high solubility in aqueous media, the simple procedure (for the pre-treatment, during preparation, and post-treatment steps), and the cost-effectiveness in comparison to other inputs like $CaCl_2$, $NaHCO_3$ or NH_4HCO_3[7,12].

2. EXPERIMENT

2.1. Chemicals

Calcium oxide (CaO), sodium carbonate (Na_2CO_3), ethanol (C_2H_5OH), ethylene diamine tetraacetic acid (EDTA), and eriochrome black T (ETOO) with analytic grade were purchased from Xilong Scientific Co., Ltd. (China) and used directly without any further purification.

2.2. Preparation of $CaCO_3$ NPs

First, $Ca(OH)_2$ solution was prepared by completely dissolving 25.0 g of CaO in 1 L of deionized water in a 2-L beaker. The beaker was placed on a magnetic stirrer, and the solution was kept stirring for various durations (4, 6, 8, 10, and 24 hours) at different stirring speeds (200, 300, 400, 500, and 600 rpm). After the dissolution, the solution was then stabilized for 30 min. before being filtered by a Buchner funnel to isolate the impurities from the $Ca(OH)_2$ solution (solution A). The concentration of Ca^{2+} in the as-prepared solution A was determined by the complexometric titration with the EDTA solution in the ETOO indicator. Similarly, solution B was also prepared by completely dissolving 47.3 g of Na_2CO_3 in 1 L of deionized water in another 2-L beaker. The solution was stirred for 1 hour at a speed of 400 rpm. After that, $CaCO_3$ NPs were synthesized by equimolar mixing of solution A and B in a 5-L beaker. The mixtures were agitated for 1 hour at a speed of 400 rpm. Consequently, the mixtures were kept stabilized for 30 min, then filtered using the Buchner funnel and washed several times with deionized water and ethanol to obtain the final $CaCO_3$ NPs.

2.3. Material characterization

The obtained product was firstly examined by thermal gravimetric analysis and differential scanning calorimetric (TGA/DSC) on a Labsys Evo equipment by SETARAM (France). The structure and phase of $CaCO_3$ NPs were then assessed by X-ray diffraction using a D8 Advance Diffractometer (Bruker, Germany). The morphology and shape of $CaCO_3$ samples were captured on scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) using a S-4800 model by Hitachi (Japan). The elemental analysis of $CaCO_3$ NPs was then evaluated using X-ray dispersion spectroscopy (EDS) method on an equipment connected to SEM. The functional groups of obtained products were also determined by the Fourier-transform infrared (FTIR) using a Shimadzu spectrometer within 400 - 4000 cm^{-1} range.

3. RESULTS AND DISCUSSION

3.1. The influences of stirring process on the solubility of CaO precursors for preparation of $Ca(OH)_2$

The dissolution of CaO in water to form $Ca(OH)_2$ was a kinetic process that depended on stirring rate, stirring duration, the grain size of CaO precursors, and temperature. The adjustment of grain size and temperature would be considered in other work since these factors could directly affected the stability of obtained products. On the other hand, in this study, the effects of stirring rate and stirring duration on the concentration of obtained $Ca(OH)_2$ solution would be evaluated.

Table 1 reports the resulted $Ca(OH)_2$ concentration ($[Ca(OH)_2]$) with different stirring speeds and durations.

Table 1. *The concentration of obtained $Ca(OH)_2$ at various stirring speeds and durations*

No.	**Feeding**		**Stirring duration**	**Stirring speed**	**$[Ca(OH)_2]$**
	CaO	deionized H_2O			
	g	mL	hours	rpm	mol/L
1	25	1000	4	400	0.079 ± 0.002
2	25	1000	6	400	0.091 ± 0.004
3	25	1000	8	400	0.112 ± 0.002
4	25	1000	10	400	0.112 ± 0.005
5	25	1000	24	400	0.111 ± 0.002
6	25	1000	8	200	0.072 ± 0.003
7	25	1000	8	300	0.098 ± 0.002
8	25	1000	8	500	0.112 ± 0.005
9	25	1000	8	600	0.113 ± 0.002

Based on the obtained data, $[Ca(OH)_2]$ increased from 0.079 mol/L up to a maximum of 0.112 mol/L as the stirring duration increased from 4 to 8 hours and insignificantly changed as elongated the duration (to 24 hours) of stirring process. If the stirring duration was not enough (≤ 8 hours), the contact time between CaO particles and water, as well as the dispersion of CaO particles in water, was insufficient, leading to incomplete dissolution. On the other sides, if the stirring duration exceeded 8 hours, because of the saturation of $Ca(OH)_2$ solution, an equilibrium was firmly settled (Eq. 1). Consequently, the elongation of stirring duration was unnecessary due to the ineffective energy consumption[7,8].

Additionally, the stirring speed was another factor that had an impact on the contact between CaO particles and water for the dissolution. The increase of stirring speed facilitated the possibility of CaO contacting water molecules, hence, promoting the dissolution of CaO in water. From obtained results in Table 1, $[Ca(OH)_2]$ grew from 0.072 mol/L at a stirring speed of 200 rpm to 0.112 mol/L at 400 rpm, and showed no significant change (to 0.113 mol/L) for further rising of speed up to 600 rpm. Therefore, the stirring speed would be adjusted to 400 rpm for an effective $Ca(OH)_2$ preparation step.

3.2. Characterization of prepared $CaCO_3$ NPs

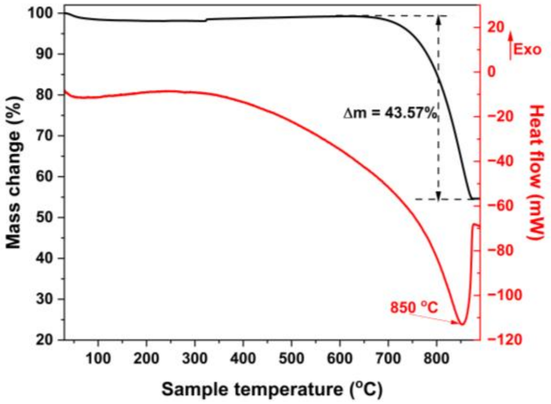


Figure 1. *Thermal analyses of $CaCO_3$ sample*

Fig. 1 described the thermal analysis of the obtained $CaCO_3$ samples. A slight change of about 1.6 wt% observed at temperatures below 200 ^{o}C was due to the evaporation of absorbed water on the surface of $CaCO_3$ particles. Further increase in temperature up to 600 °C resulted in insignificant mass changes of analyzed sample. The remarkable lost in mass of 43.57 wt% occurred between 600 °C and 860 °C, corresponding to an endothermic process from about 400 °C to 880 °C with the peak at 850 °C. This process was attributed to the thermal decomposition of $CaCO_3$ into CaO and CO_2, as the lost of 43.57 wt% due to the evaporation of CO_2. This behavior was characteristic of the stable calcite phase of $CaCO_3$ NPs. It also indicated a high purity of obtained $CaCO_3$ NPs without the presence of aragonite or vaterite phase, which were decomposed at the lower temperatures[10,11].

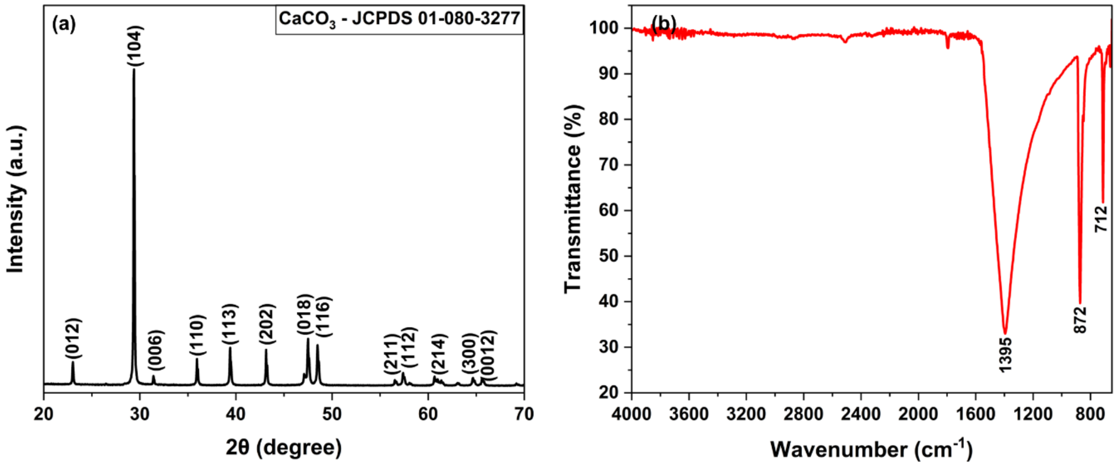
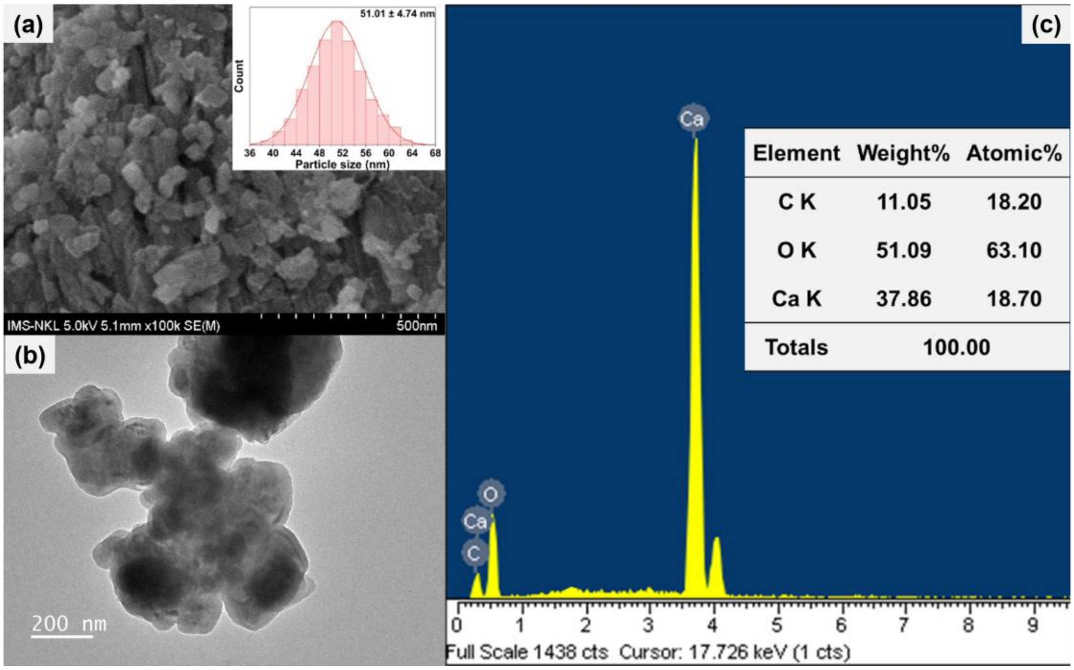


Figure 2. *(a) XRD and (b) FTIR curves of prepared $CaCO_3$ sample.*



Element	Weight%	Atomic%
C K	11.05	18.20
O K	51.09	63.10
Ca K	37.86	18.70
Totals	100.00	

Figure 3. *(a) SEM (inset: particle size distribution), (b) TEM images, and (c) EDS spectra of $CaCO_3$ NPs.*

The XRD technique was then employed to determine the crystalline phase of obtained $CaCO_3$ NPs (Fig. 2a). The diffraction peaks were assigned to the corresponding planes, which coincided with the standard card JCDPS No. 01-080-3277. The formation of calcite phase with the absence of vaterite and aragonite phase was once confirmed by the sharp diffraction peaks at 29.4^o, 39.4^o, and 43.4^o[13]. From obtained XRD data, the Scherrer equation was applied for the calculation of the crystalline sizes for obtained $CaCO_3$ NPs[14]. The calculated crystalline sizes of examined $CaCO_3$ sample ranged from 37.39 nm to 64.63 nm (an average of 51.01 ± 4.74 nm).

The FTIR spectra described the characteristic peaks at 1395 cm^{-1}, 872 cm^{-1}, and 712 cm^{-1} (Fig. 2b). These peaks were ascribed to the stretching asymmetric vibration of C = O bond in carbonate (CO_3^{2-}), the out-plane and in-plane distortion vibration of C-O bonds, respectively[8,10]. This also stated that the $CaCO_3$ NPs existed in the stable calcite phase. In addition, no characteristic signals of OH^- of $Ca(OH)_2$ or HCO_3^- of $NaHCO_3$ were detected in the FTIR spectra. Moreover, the signal due to the vibration of Ca-O appeared at the wavenumber < 700 cm^{-1}.

According to the material analyses, the preparation procedure of $CaCO_3$ NPs in this study was well-controlled, and prior to obtaining the calcite phase with high purity[9,11]. It was so meaningful since the calcite phase was the most thermal, chemically, and mechanically stable form of $CaCO_3$ that was compatible with the applications in medicine, additives in composites, as well as environmental treatment[10,11].

The morphology of obtained $CaCO_3$ NPs was captured by the SEM and TEM. It could be seen that the formation of uniform cubic-like particles with the size of 50 - 100 nm (Fig. 3a), which was also in agreement with the calculated results obtained from XRD curve. However, the aggregation of $CaCO_3$ NPs also happened, leading to the large bulks (less than 200 nm) as displayed on the TEM images (Fig. 3b). The EDS coupled with the SEM also exhibited the elemental composition of obtained $CaCO_3$ samples (Fig. 3c). The finding confirms the presence of Ca, C, and O in the product with the atomic percentages of 18.70%, 18.20%, and 63.10%, which was analogous with the feeding. Besides, no impurities, such as Na^+ or Cl^- were presented in the final products, suggesting that the purification step effectively removed the residues or the by-products[12].

4. CONCLUSION

In this study, a procedure for the synthesis of $CaCO_3$ NPs using the precipitation method was introduced. To ensure the high purity of the $CaCO_3$ product, the conditions for $Ca(OH)_2$ preparation from CaO precursor, including the stirring rate and stirring duration, were controlled with the optimal parameters of 400 rpm and 8 hours, respectively. Materials characterization later confirmed the formation of calcite phase for $CaCO_3$ with a high purity and uniform cubic-like particles of ≤ 200 nm in size. This suggested that the obtained $CaCO_3$ products could be used for specific purposes in medicine, catalysis, environmental treatment, and others.

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Declaration: This is the original work and has not been submitted to any journal. The authors declare no conflicts of interest.

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