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Synthesis of Calcium Carbonate ($CaCO_3$) from Eggshell by Calcination Method

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Abstract

Calcium is an essential nutrient the human body needs to control blood pressure and maintain strong bones and teeth. One type of calcium that is often consumed and safe for health is calcium carbonate. It can obtain this material from chicken eggshell waste, where it is known that the $CaCO_3$ content is 95%. Therefore, it conducted this research to see the phase, functional group, absorbance level, and energy band gap of $CaCO_3$ samples. $CaCO_3$ was synthesized using the calcination method, in which the egg shells were first soaked in sodium hypochlorite, then dried at 250°C for 10 minutes, and $CaCO_3$ powder was obtained. Then the powder was characterized by XRD, FTIR, and UV-Vis. The results of XRD analysis showed that the calcite phase of $CaCO_3$ was 100% according to the JCPDS PDF of calcite (96-901-6707) with a crystalline size of $CaCO_3$ of 22.6 nm. The results of FTIR of $CaCO_3$ samples at the absorption peak of 4000-500 cm^{-1} identified the functional groups of Ca-O, C-O, $-CH_2$, and O-H. $CaCO_3$ samples can absorb light at wavelengths of 237.1 nm, 251.5 nm, and 289.7 nm, which have an energy band gap of 3.91 eV. Thus, using this simple calcination method, the $CaCO_3$ sample obtained from the extraction of chicken egg shells can later be applied in the medical field.

Introduction

Calcium is a nutrient humans need to support essential bodily functions, such as controlling blood pressure, regulating blood clotting, muscle contraction, maintaining a stable heart rate, and maintaining strong bones and teeth. When the calcium requirement of the human body is too low, it will take calcium in the bones to maintain normal blood calcium, which is very bad for human bone health. It can fulfill calcium in the human body from various sources of calcium derived from animal products, vegetables, and food waste [1]. Four types of calcium are often consumed in the community, namely, calcium carbonate (40% calcium), calcium citrate (21% calcium), calcium lactate (13% calcium), and calcium gluconate (9% calcium). The polymorphic properties of $CaCO_3$ consist of aragonite, vaterite, and calcite. The metastable phase of calcium carbonate lies in the aragonite and vaterite phases. This aragonite phase has an orthorhombic crystal structure, while vaterite has a hexagonal crystal structure [2]. $CaCO_3$ material is an inorganic calcium salt most often used in the health sector because it has properties that are easy to absorb and neutralize acids and are easily obtained from several natural resources such as limestone, clam shells, and egg shells from several poultry animals [3]

Chicken egg shells have a high potential to become waste because eggs are a source of protein for humans. So far, only the yolk and white of the egg have been used. At the same time, the shell is thrown away without any further use. Even the covers of chicken eggs cannot be decomposed by soil microbes, which impacts increasing environmental pollution [4]. From the chemical aspect, chicken eggshells consist of water (2%) and several protein fiber networks such as calcium carbonate phase calcite (94%), calcium phosphate (1%), magnesium carbonate (1%), and other organic substances (2%) [5]. Several studies have shown that the availability of $CaCO_3$ in chicken eggshells is much higher than that of oyster shells [1]. Chicken egg shells mostly have 95% $CaCO_3$ in the calcite phase, producing the best natural $CaCO_3$ compared to $CaCO_3$ from oyster shells and commercial calcium carbonate [3]. There are several methods of $CaCO_3$ extraction, including ball milling, leaching, and dry oven. The ball milling method requires equipment that is quite expensive, as was done [6] where in his research, he produced 95.7% aragonite phase $CaCO_3$ from blood clam shells. The leaching method in $CaCO_3$ synthesis from dolomite only requires CO_2 gas flow and high-temperature calcination (800^oC) for 8 hours. However, the synthesis results contained two phases of $CaCO_3$, calcite, and vaterite, with a percentage of 87.31% and 12.69%, respectively [7]. The study [8] used the dry oven method with a temperature of 70°C for 24 hours to synthesize $CaCO_3$ from chicken egg shells. However, this study obtained only 97.17% of the $CaCO_3$ calcite phase. Based on the research data above, in this study, the synthesis of $CaCO_3$ from chicken egg shells used a simple calcination method at 250°C for 10 minutes. This method does not require CO_2 gas flow and high temperatures but only requires a dry oven which does not require expensive equipment, so in this synthesis, it is expected to produce 100% calcite $CaCO_3$ phase. Characterizations such as XRD, FTIR, and UV-Vis were carried out to determine the characteristics of $CaCO_3$ from chicken eggshells, such as phase, functional groups, absorbance, and energy band gap. The $CaCO_3$ material synthesized from this research is expected to be later applied in the medical field.

Experimental Method

The equipment used in this research includes a 2000 mL beaker, 50 mL crucible, furnace, 200 mesh sieve, spatula, digital balance, dry oven, stainless steel mortar, and pestle. The materials used in this study included chicken eggshell waste, Merck 105614 sodium hypochlorite solution 6-14%, and distilled water.

The steps for synthesizing $CaCO_3$ using the calcination method are the shells of chicken eggs are washed with flowing water, dried in the sun, and then soaked in sodium hypochlorite solution for 6 hours. Furthermore, the egg shells were dried at 250°C for 10 minutes and then crushed and mashed using a stainless-steel mortar pestle. Moreover, the eggshell powder was sieved using a 200-mesh sieve to increase the white fine powder's surface area and equalize the powder particles' size. The synthesized powder was then characterized by XRD, FTIR, and UV-Vis Spectrophotometer to determine the phase structure, functional groups, and absorbance of $CaCO_3$ samples from chicken eggshell waste.

XRD (X-Ray Diffraction) characterization was carried out with (Cu) 40 kV, 35 mA, a wavelength of 1.541784, and an angle of 2θ between 10^o to 90^o. This XRD uses the

PanAnalytical brand with the Expert Pro type. The XRD characterization data were analyzed using the Match software by matching the presence of the diffraction peaks formed in the diffractogram graph according to the JCPDS data listed in the Match software. In the XRD graph results, the size of the crystals formed can be calculated using the Debye Scherrer equation [6].

$$D = \frac{(0,9)\lambda}{B\cos\theta} \qquad (1)$$

Where D is the crystal diameter (µm), B is the peak width at half maximum (Full-Width Half Maximum), is the wavelength (0.15418 nm), and is the diffraction angle. Characterization of FTIR (Fourier Transform Infra-Red) to determine the functional group. It is characterized by absorption peaks indicating the chemical bonds of atoms in the sample. The FTIR test used the Shimadzu brand IRPrestige 21 types with an absorption peak of 4000 to 500 cm^{-1}. Characterization of UV-Vis (Ultra Violet Visible) spectrophotometer to determine the level of absorbance indicated by the peak data for UV absorption and the energy band gap of $CaCO_3$. The results of the absorption rate of the UV-Vis spectrophotometer can be calculated energy band gap using Tauc's Plot equation [9].

$$\alpha h v = A\left(h v - E_g\right)^n \qquad (2)$$

Where is the absorbance coefficient ($^{2.303}/_{A}$), h is Planck's constant, v is the photon frequency, E_g is the energy band gap (eV), A is the wavelength (nm), with n=2. The UV-Vis spectrophotometer was tested using the Genesys 10S UV-Vis v4.003 2L9P286007 brand from 200 to 1000 nm.

Result and Discussion

X-Ray Diffraction (XRD) Characterization Results

The X-Ray Diffraction (XRD) characterization data was obtained as a graph of the diffraction peak, which was then analyzed using Match software. The results of the analysis show that each diffraction peak is at an angle of 2θ, namely: 23.0°; 29.4°; 31.5°; 36.0°; 39.4°; 43.2°; 47.6°; 48.6°; 56.6°; 57.5°, with Miller index (012), (104), (006), (110), (113), (202), (018), (116), (211), and (122) indicated $CaCO_3$ calcite phase by 100%. The diffraction peak data on the synthesis results are the following JCPDS PDF number 96-901-6707. The diffraction peak 2θ = 29.4° with Miller's index (104) shows the same rise according to the results of [1].

In this study, using a temperature of 250°C for 10 minutes to synthesize $CaCO_3$ from chicken egg shells produced a calcite phase of $CaCO_3$ of 100%. In contrast to that carried out [11] where the $CaCO_3$ compound from chicken eggshells is made at a high temperature of 1000°C for 5 hours, and even then, it still contains impurities in the form of CaO. Likewise, in research [12], the use of temperatures of 550°C, 650°C, and 750°C for 4 hours resulted in the percentage of calcite $CaCO_3$ of 98.8%, 92.2%, and 84.0%. The crystal size of $CaCO_3$ can be measured using the Debye Scherrer formula in equation (1), and the average size of $CaCO_3$ crystals is 22.6 nm with a nanocrystalline character with a crystalline size below 100 nm [13].

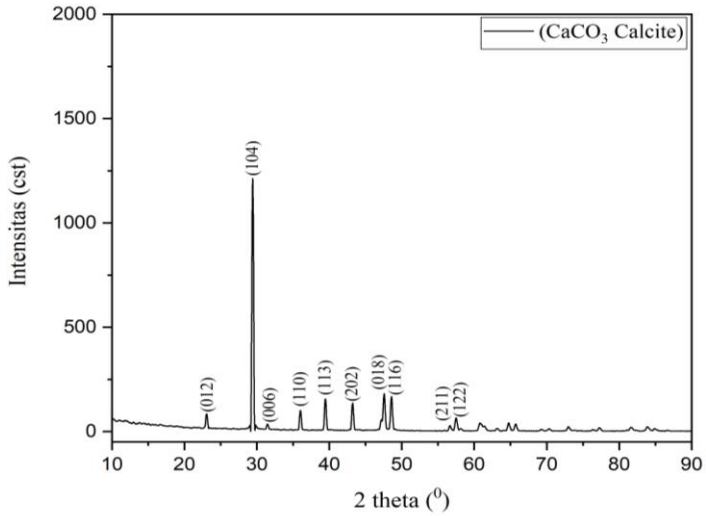

Figure 1. XRD diffraction pattern of $CaCO_3$ sample from chicken eggshell synthesis

Fourier Transform Infra-Red (FTIR) Characterization Results

The FTIR spectrum of the $CaCO_3$ sample is obtained in the form of a graph that relates the wave number to its transmittance, located at the absorption peak of 4000-500 cm^{-1}. The FTIR spectrum of the $CaCO_3$ sample in Figure 2 is generated by the absorption of electromagnetic radiation which has absorption peaks at 3275.1 cm^{-1}, 2980.0 cm^{-1}, 2873.9 cm^{-1}, 2513.2 cm^{-1}, 2140.9 cm^{-1}, 1795.7 cm^{-1}, 1651.1 cm^{-1}, 1433.1 cm^{-1}, 1083.9 cm^{-1}, 875.7 cm^{-1}, and 711.5 cm^{-1}.

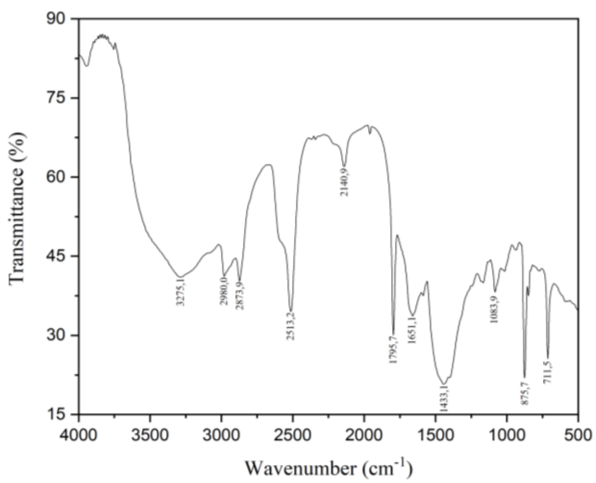

Figure 2. FTIR spectrum of $CaCO_3$ sample from chicken eggshell synthesis

At the absorption peak of 3275.1 cm^{-1}, there is an O-H stretching bond [14], while at the absorption peak of 2980 cm^{-1} and 2873.9 cm^{-1}, there is an asymmetric $-CH_2$ bond and symmetric stretching [15]. The HCO_3 bond is located at the absorption peak of 2513.2 cm^{-1} [15]. The decrease in absorption intensity at wave number 1795.7 cm^{-1} is due to the constant increase in $CaCO_3$ concentration, which is indicated by the vibration of the stretching Ca-O bond [16]. The presence of Ca-O bonds asymmetric stretching [16], C-O anti-symmetric stretching [17], and CO_3^{2-} symmetric stretching [17] is located at the absorption peak of 1651.1 cm^{-1}, 1433.1 cm^{-1}, and 1083.9 cm^{-1}. The $CaCO_3$ calcite phase is identified at 875.7 cm^{-1} with CO_3^{2-} bonds [16], and there are Ca-O bonds at the peak of 711.5 cm^{-1} [14]. For more details, the results of the FTIR $CaCO_3$ characterization can be seen in the following table:

Table 1. Types of bonds of $CaCO_3$. absorption peaks

No.	$CaCO_3$ synthesis (cm^{-1})	Peak reference (cm^{-1})	Bond type	Reference
1	711.5	713	Ca-O	[2]
2	875.7	876	CO_3^{2-}	[3]
3	1083.9	1082	CO_3^{2-} symmetric stretching	[4]
4	1433.1	1421	C-O *anti-symmetric stretching*	[4]
5	1651.1	1511	Ca-O *asymmetric stretching*	[3]
6	1795.7	1798	Ca-O *stretching*	[3]
7	2513.2	2517	HCO_3	[5]
8	2873.9	2875	$-CH_2$ *symmetric stretching*	[5]
9	2980.0	2925	$-CH_2$ *asymmetric stretching*	[5]
10	3275.1	3628	O-H *stretching low concentration of* $Ca(OH)_2$	[2]

Characterization Results of Ultra Violet Visible Spectrometer (UV-Vis Spectrophotometer)

The UV-Vis spectrophotometer was characterized to determine the level of absorbance at specific wavelengths and the energy band gap of $CaCO_3$. Figure 3 and Figure 4 show the absorbance spectrum of $CaCO_3$ at a wavelength of 200-500 nm and the energy band gap of $CaCO_3$.

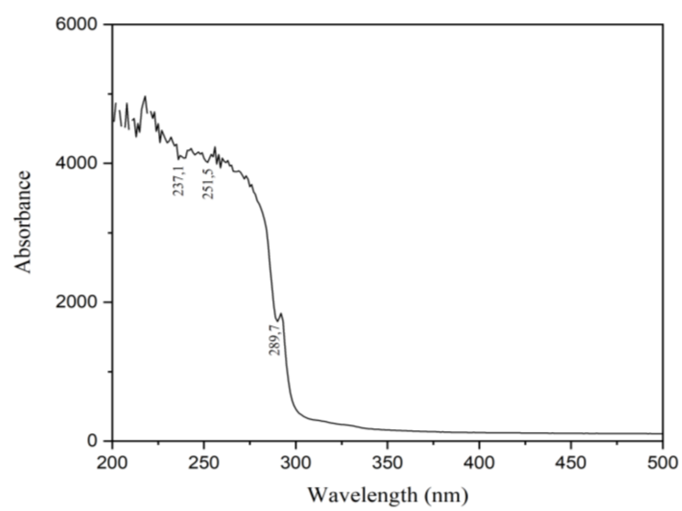

Figure 3. Absorbance spectrum of $CaCO_3$ sample from chicken eggshell synthesis

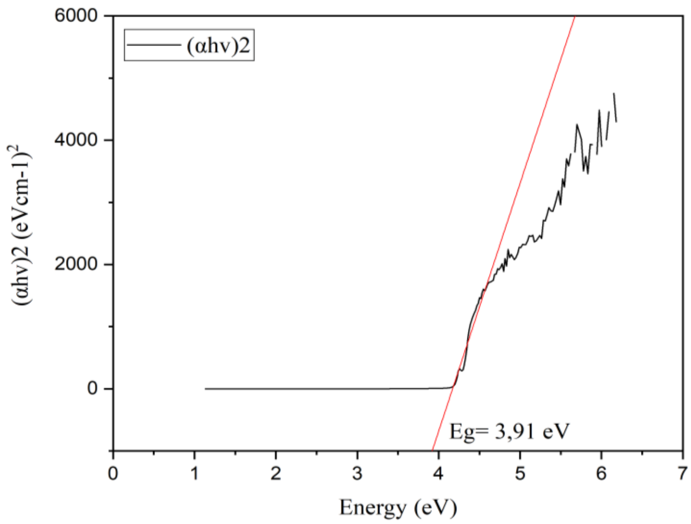

Figure 4. The energy band gap of $CaCO_3$ sample from chicken eggshell synthesis

Figure 3. shows the absorption rate of $CaCO_3$ from the synthesis of chicken egg shells in the range of 237.1 nm, 251.5 nm, and 289.7 nm following previous studies conducted [18] reporting that the absorption rate of $CaCO_3$ in the calcite phase located at 220 nm, 252 nm, and 341 nm. Figure 4 shows a graph of the calculation results of the Tauc Plot equation in equation (2); photon energy on the x axis gives the energy band gap of $CaCO_3$ (E_g) is 3,91 eV which is larger than the previous study [19], shows that the energy band gap of $CaCO_3$ from limestone synthesis is 3, 15 eV. However, the energy band gap of $CaCO_3$ in this synthesis is smaller than the calculations previously reported by [9] on the synthesis of $CaCO_3$ in the calcite phase using the microemulsion technique.

Conclusion

Based on the results and discussion in this study, the $CaCO_3$ sample was successfully synthesized using the calcination method at a temperature of 250^{o}C with a holding time of 10 minutes. The results of XRD characterization obtained 100% calcite $CaCO_3$ phase, according to JCPDS PDF calcite data (96-901-6707). The $CaCO_3$ sample had Ca-O, C-O, -CH_2, and O-H functional groups at an absorption peak of 4000-500 cm-1. Calcium carbonate produced by the synthesis of chicken egg shells has been proven to absorb light at specific wavelengths with an energy band gap of $CaCO_3$ with an energy band gap of 3.91 eV.

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