

Review of Structural Characterization of Calcium Carbonate (CaCO_3) Using Electron Microscopy: Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM)

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ABSTRACT

This review aims to provide an in-depth explanation of how to characterize the structure of currently prepared calcium carbonate (CaCO_3) materials using a Scanning Electron Microscope (SEM) and a Transmission Electron Microscope (TEM). The study method was Systematic Literature Review (SLR). From the results, SEM and TEM electron microscopy methods are known to be very effective and very useful for characterizing the structure of CaCO_3 materials because of their successfulness in accurately determining the morphology, size, and agglomeration of CaCO_3 materials. Most of the morphological forms of pure CaCO_3 are also known to be spherical and some of them are cubic. Determination of this structure is useful so that the design criteria for the application of CaCO_3 can be better designed. In the future, the results of this study are expected to be used as a basis for information in the structural characterization of CaCO_3 using SEM and TEM.

Keywords: electron microscope; CaCO_3 ; SEM; structural characterization; TEM

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INTRODUCTION

Calcium carbonate (CaCO_3) is one of the most abundant types of compounds and is widely found on the earth's surface in the form of limestone. CaCO_3 is also non-toxic and has high biocompatibility and excellent biodegradability. CaCO_3 is widely used in industry and various applications such as drug delivery, filters, adsorbents, and others (Maleki Dizaj et al., 2019; Wang et al., 2018; J. Li et al., 2016; Zhang et al., 2018).

CaCO_3 has three main crystalline forms, namely calcite, vaterite, and aragonite. Anhydrous CaCO_3 crystals will form calcite under environmental conditions and form aragonite and vaterite under certain other conditions, so calcite is the most common calcium carbonate polymorph found in nature. In nature, the crystallization of CaCO_3 is usually initiated by the formation and further transformation of amorphous CaCO_3 (Miyazaki, Arie, and Shirotsuki 2019; Kezuka et al., 2018). Calcite and aragonite are the most stable forms and have a trigonal and orthorhombic polymorphic crystal form, while vaterite is the least stable form and has a hexagonal crystal form. Calcite is generally cubic and scaly in shape, while porous vaterite has a spherical morphology with a specific surface area and abundant pore structure, but this vaterite is easily converted to calcite in acidic or basic solutions at high temperatures (Mahmood et al., 2017; Ševčík et al., 2015; Kogo, Umegaki, and Kojima, 2019; Pérez-Villarejo et al., 2018; Qiao et al., 2017; Shi et al., 2017; Tolba et al., 2016).

In its application as a bone substitute, pure and porous vaterite is preferred to enhance the formation of apatite carbonates. In addition, the porous CaCO_3 microparticles also have the



potential to be a promising heavy metal adsorbent. This is due to the heavy metal separation capacity depending on the surface morphology and surface chemistry. This porous CaCO_3 has a higher surface area, is easier to separate by filtration/centrifugation, and the synthesis is easy and fast (Cahyanto et al., 2012; Ma et al., 2012). Thus, the structural characterization of CaCO_3 is very important so that the desired material criteria can be obtained and the application is more precise.

The structural characterization of CaCO_3 can be carried out using the Electron Microscopy (EM) method. EM is a tool that serves to study the morphological features and ultrastructural examination of various materials, especially the Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) (Klang et al., 2012; Fan et al., 2019). The interaction between the material and the electron beam in EM will produce an electron micrograph which is then processed into an image. These interactions can be influenced by several factors, including electron energy, material density, element atomic number, and material surface topography. Electron interactions which can be either elastic or non-elastic interactions in material atoms will generally produce different forms such as secondary electrons and backscattered electrons. SEM will produce an image of the sample surface resulting from the electron beam scattered across the sample surface, while TEM will produce a two-dimensional projected image of the sample resulting from the electron beam that penetrates the sample (Rehn et al., 2018; Suga et al., 2014; Susi et al., 2019).

Several researchers have characterized various structures of CaCO_3 using several types of SEM and TEM. CaCO_3 with spherical morphology can be identified using general SEM and TEM by many researchers (Febrida et al., 2021; Zhang et al., 2018; S. Li et al., 2019), while CaCO_3 with chain/spheroidal morphology was identified through Field Emission-SEM (FE-SEM) and TEM, in addition to the irregular agglomerate state was also seen through Cyro-SEM (Kezuka et al., 2018). Cubic CaCO_3 can also be identified using FE-SEM and TEM (L. Li et al., 2020). These findings will be discussed further in the next section.

Unfortunately, data collection related to the determination of the structure of CaCO_3 using the EM method has not been carried out in a more comprehensive and in-depth manner. Therefore, in this chapter, the determination of CaCO_3 structure using SEM and TEM will be discussed further through the Systematic Literature Study (SLR) of several journal articles. This study will present a comprehensive and in-depth review of the determination of CaCO_3 structure in the last 5 years.

METHOD

The structural characterization of CaCO_3 using SEM and TEM in this study was investigated through a Systematic Literature Review (SLR) method. SLR is a research method and process for identifying and critically assessing relevant research, as well as for collecting and analyzing data from that research. The purpose of the SLR is to identify all the empirical evidence that fits the pre-determined inclusion criteria to answer a particular research question or hypothesis. By using explicit and systematic methods when reviewing articles and all available evidence, bias can be minimized, thereby providing reliable findings from which conclusions can be drawn and decisions made (Snyder, 2019).

The journal articles reviewed in this study were searched through various search media and journal publications such as Google Scholar, Science Direct, Springer, and MDPI. The keywords used to browse these articles include CaCO_3 structural characterization using SEM and TEM, electron microscopy, SEM and TEM of CaCO_3 , and CaCO_3 structural characterization. Articles searched are in the 2018-2024 publishing year.

The articles being searched were selected according to the following criteria.

1. Articles must contain information related to pure CaCO_3 without any kind of dopants or composites.
2. The article contains information regarding the porous structure of CaCO_3 .
3. SEM and TEM information on CaCO_3 was in the same article.

Articles that have met these criteria are selected and presented in Table 1. The journal quality is based on Scimago Journal Rank (SJR).

Table 1 Article Selection Results

No.	Year	Title	Quality	Reference
1.	2021	Synthesis and Characterization of Porous CaCO ₃ Vaterite Particles by Simple Solution Method	Q2	(Febrida et al., 2021)
2.	2020	Porous Calcite CaCO ₃ Microspheres: Preparation, Characterization, and Release Behavior as Doxorubicin Carrier	Q1	(L. Li et al., 2020)
3.	2019	The Mn-Promoted Double-Shelled CaCO ₃ Hollow Microspheres as High Efficient CO ₂ Adsorbents	Q1	(S. Li et al., 2019)
4.	2018	Effective Removal of Toxic Heavy Metal Ions from Aqueous Solution by CaCO ₃ Microparticles	Q2	(Zhang et al., 2018)
5.	2018	Calcium Carbonate Chain-like Nanoparticles: Synthesis, Structural Characterization, and Dewaterability	Q1	(Kezuka et al., 2018)

RESULT AND DISCUSSION

In this section, the literature review and state of the art of SEM and TEM uses to characterize the structure of CaCO₃ will be presented and discussed.

Electron Microscope Principles

In EM, it is the electron beam that is used to form an image of the specimen. EM is operated in a vacuum by focusing the electron beam. The image will be enlarged using the help of an electromagnetic lens. When compared to the wavelength of visible light ($\lambda = 400\text{-}700\text{ nm}$), the electron wavelength used in EM is much shorter (e.g., $\lambda = 0.005\text{ nm}$ at an accelerating voltage of 50 kV). In EM, the wavelength and resolution will decrease as the accelerating voltage increases. The two most common types of EM are SEM and TEM. SEM and TEM are one of the most widely used tools for microstructural characterization of materials because the images they produce are very detailed. SEM and TEM are ideal for use in determining elemental microanalysis and particle characterization as well as high-resolution images so that information such as topography, morphology, composition, and material microstructural information can be obtained (Polman et al., 2019; Shah, 2013).

1. Scanning Electron Microscope (SEM)

In H. Stintzing's patent in 1927, the idea for SEM first appeared intending to determine the size of small particles that cannot be detected by light microscopy. This idea begins with irradiating the sample using a narrow-collimated beam, such as light or x-rays, then the sample is moved transversely to the beam. The interaction between the light and the sample is measured using a sensitive recording device, then amplified and displayed on an electron tube. Unfortunately, this method does not produce a zoomable image. In 1935, the first electron-beam scanner was developed by H. Knoll. The scanner can produce an image of the surface of the bulk sample using the emitted secondary electrons. In the following decades, SEM has developed and been used for surface imaging of materials in a wide variety of different fields. Today, SEM is a well-established method for use in the surface characterization of materials under both ultra-high vacuum, high vacuum, and low vacuum conditions.

Figure 1 shows a schematic of the SEM instrumentation. In general, SEM consists of two main parts, namely the microscope column and the electronic device. The microscope column consists of an electron gun consisting of a cathode, Wehnelt cylinder, and anode components, one or two condenser lenses, two pairs of beam deflection coils, an objective lens, and several apertures. The specimen holder is located at the lower end of the microscope column and there is also a detector for the different signals generated by the electron-specimen interaction. The microscope column and specimen chamber are evacuated using a combination vacuum pump and a high vacuum pump (usually a turbomolecular pump). The pressure in the specimen chamber is usually about 10^{-4} Pa , allowing the electron beam to move from the cathode to the specimen with little interaction with the residual gas molecules. The electronic device consists of an electric power supply for the accelerating voltage (typical range is about 0.5-30 kV) as

well as a condenser and objective lens, a scanner generator, and an electronic amplifier for the various acquired signals. In addition, the device also houses one or more Liquid Crystal Display (LCD) monitors for displaying a graphical user interface and live or recording images. Electron beam, selected signal, and image recording can be controlled via keys and computer keyboard.

The electron beam emitted from the cathode and accelerated by a voltage of 0.5-30 kV between the cathode and anode will form the smallest beam cross-section near the anode with a diameter of about 10-50 m. This point size is too large to produce a sharp image. Therefore, the crossover is minimized by a lens system consisting of one or two condenser lenses and an objective lens and is focused on the specimen surface. Most SEMs can produce an electron beam having the smallest dot size of about 5-10 nm and an electron probe current in the range of 10^{-12} - 10^{-10} A, which is sufficient to form an image with a reasonable Signal-to-Noise Ratio (SNR). For the higher probe currents required for some modes of operation, the smallest probe spot size increases to 100 nm or more. The objective lens has a relatively long variable focal length which allows a large working distance (this corresponds to the distance between the specimen and the lower pole piece) in the range of about 2-50 mm. This ensures that the various signals generated by the impinging beam electrons in the small specimen interaction volume can be collected by a detector located laterally above the specimen with sufficient efficiency. A pair of beam deflection coils located in front of the objective lens and controlled by the scanner generator scans the electron probes line by line across a small area of the specimen. The detected signals are then collected and recorded via a graphical user interface on the computer monitor screen. The signal may vary from location to location because the electron-specimen interactions vary due to, for example, the topography and composition of the specimen. The magnification of the image is given by the ratio of the scan length on the monitor and the corresponding scan length on the specimen, for example, increasing the magnification can be easily achieved by reducing the deflection coil current in the microscope column, i.e., lowering the scan length on the specimen and keeping the image size on the monitor constant. The magnification also depends on the working distance; however, modern SEM compensates for each working distance automatically so that the correct magnification displayed is maintained (Klang et al., 2012; Vos et al., 2014; Newbury and Ritchie, 2013; Brodusch et al., 2021; Shah, 2013).

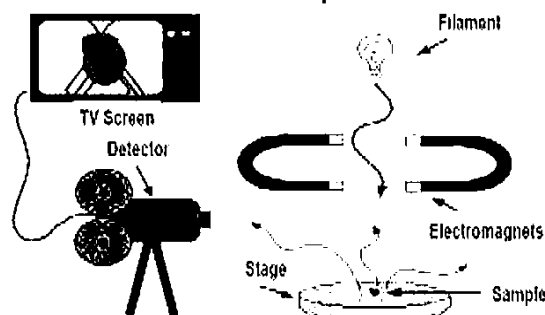


Figure 1 SEM instrumentation schematic (Figure was adopted from Shah, 2013)

2. Transmission Electron Microscope (TEM)

The prototype TEM was developed by Ernst Ruska and Max Knoll. This prototype is capable of magnification up to 400 times and the principles of electron microscopy are also demonstrated on this prototype. In 1934, the separation power of electron microscopes surpassed optical microscopes, then the first commercial electron microscope was produced in 1939 by Siemens based on Ruska's design. Recently, successful completion and testing of the electron-optical components required for direct correction of spherical aberrations present in all electromagnetic spherical lenses has been achieved. From early corrector designs for TEM based on two hexapole elements combined, several more complex designs have emerged that are capable of

correcting axial and off-axis aberrations and most recently first-order chromatic aberrations. The instrumentation scheme of TEM is shown in Figure 2.

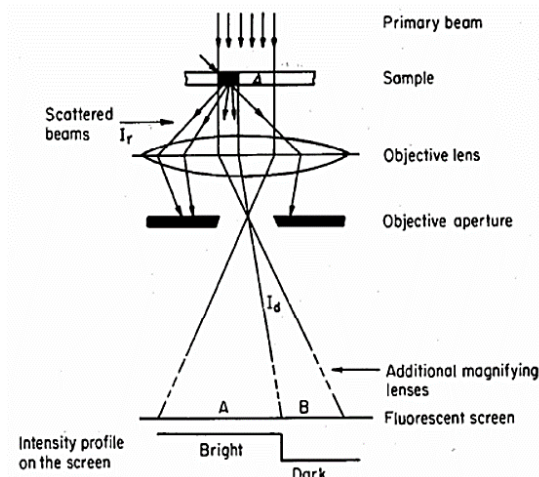


Figure 2 TEM instrumentation schematic (Figure was adopted from Shah, 2013)

TEM uses electrons instead of light and electron magnetic lenses instead of glass lenses. The accelerated electrons from the electron source are focused into a small, uniform beam by the condenser lens. Small condenser openings are used to exclude electrons that move at a large angle to the optical axis. The beam then traverses the sample. The portion of the diffraction beam depends on the thickness and electron transparency of the sample. The transmitted light is then focused by the objective lens to form an image. This image is then enlarged by an intermediate lens and projector onto a phosphor screen or electron camera. The aperture of the objective lens can be used to increase the contrast of the image by allowing only part of the beam of light to be transmitted or diffracted, or both. After passing through the sample, the beam in the same direction is focused onto the same point in the rear focal plane of the objective lens, which produces an electron diffraction pattern. All electrons scattered from the same sample point are ideally focused on the same point in the image plane. In practice, due to lens aberration and the small angle of reception of the lens, the dots are more like blurry discs, even though the discs are very small. For electron diffraction, the focus of the intermediate lens is changed (by changing the current in the lens), so that the rear focal plane of the objective lens becomes the object plane for the intermediate lens. This method then allows electron images and diffraction patterns to be recorded from the same sample area, only by changing the power of the lens, which is one of the main advantages of TEM (Shah, 2013; Brodusch et al., 2021; Liu, 2021).

3. Comparison of SEM and TEM

SEM produces an image with the help of secondary electrons which gives a three-dimensional impression, whereas TEM projects electrons through an ultra-thin slice of the specimen and produces a two-dimensional image. Specimens can be magnified roughly between 10 and 100,000 times in SEM and between 500 and 500,000 times in TEM. It depends on the instrument used (Brodusch et al., 2021). Table 2 presents a summary of the differences between SEM and TEM.

Table 2 Difference between SEM and TEM

Differentiating Factors	SEM	TEM
Types of Electrons	Scattering Electrons	Transmission Electrons
Electron Current	Small and Focused	Wide
Voltage	~1–30 kV	~60–300 kV
Image Dimensions	3D	2D
Image Type	Topography/Surface	Internal Structure
Resolution	Lower	Higher

Differentiating Factors	SEM	TEM
Magnification	Up to ~1–2 Millions Times	More than 50 Millions Times
Field of View	Big	Limited
Optimal Spatial Resolution	~0.5 nm	<50 pm
Sample Thickness	Free	Usually <200 nm
Sample Penetration	No	Yes
Sample Limitations	Wider	More Limited
Sample Preparation	Simpler	More Complicated
Operation	Easier	Harder
Speed	Faster	Longer
Cost	Cheaper	More Expensive

Currently Findings

Table 3 shows and summarizes some of the SEM and TEM parameters on the structural characterization of CaCO_3 . Febrida et al. (2021) characterize the morphology of CaCO_3 vaterite synthesized by the simple solution method and the morphology is known to be spherical as shown in Figure 3(a-d). The CaCO_3 particles formed secondary microspheres with nano-sized primary spherical particles and the average size of the microspheres was about $(2.91 \pm 1.06) \mu\text{m}$ for a stirring speed of 800 rpm (Figure 3(a)), and approx. $(2.47 \pm 0.85) \mu\text{m}$ for agitation speed of 1000 rpm (Figure 3(c)). The average size of the primary particles was $(153 \pm 27.95) \text{ nm}$ (Figure 3(b)) for a stirring speed of 800 rpm and $(171.29 \pm 36.61) \text{ nm}$ (Figure 3(d)) for a stirring speed of 1000 rpm. The morphology of CaCO_3 at a stirring speed of 800 rpm is denser and more rounded than the morphology of CaCO_3 at a stirring speed of 1000 rpm which is relatively irregular in shape. In addition, the average size of the microspheres is also higher at agitating speed of 800 compared to 1000 rpm, so it can be concluded that the growth rate of microspheres will be faster at lower speeds because higher speeds can prevent adsorption of nanoparticle suspensions in the growth process. spherulite to form larger nanoparticles in the presence of centrifugal force, but the movement of ions and molecules will increase so that the possibility of collisions and the rate of active interaction of vaterite with foreign ions in solution will also increase and will encourage the transformation of the vaterite phase into calcite as shown by SEM image in Figure 1.3c highlighted in the red circle (Febrida et al., 2021).

Table 3 Some applications of electron microscopy in structural characterization of CaCO_3

EM Technique/ Model	Condition	Parameter	CaCO_3 Morphology	CaCO_3 Particle Size	Reference
SEM/ Hitachi SU3500	10 kV; 90°	Morphology and Primary and Secondary Particle Size Distribution	Spherical	Microsphere: 2.91 and 2.47 μm Primary: 153 and 171.29 nm	(Febrida et al., 2021)
TEM/ Hitachi TEM System	120 kV			Primary: 150 nm	
TEM/ JEM-2100HR	200 kV	Particle Morphology	Chain/ Spheroidal	Primary: 152 nm and 34.7 nm	(Kezuka et al., 2018)
FE-SEM/ JSM-6330F	3 kV	Agglomerate Size Distribution		Chain Particles: 2.3; 4.3; and 9.8 μm Spheroidal Particles: 1.9; 3.5; and 7.1 μm	

EM Technique/ Model	Condition	Parameter	CaCO ₃ Morphology	CaCO ₃ Particle Size	Reference
Cryo-SEM/ SU6600	2 kV	Agglomeration State		Irregular Agglomerate	
SEM/ Zeiss Sigma VP FEG SEM	-	Morphology and Particle Distribution	Spherical / Cubic	2 and 10 μm	(Zhang et al. 2018)
HR-TEM/ FEI Tecnai TF20	-				
FE-SEM/ JSM-7600 F	-	Morphology and Particle Distribution	Cubic	Microsphere: 3 μm	(L. Li et al., 2020)
TEM/ JEM- 2100 F	200 kV				
SEM/ Hitachi S4800	10 kV	Morphology and Particle Distribution	Spherical	Microsphere: 1 μm	(S. Li et al., 2019)
TEM/ Tecnai G2 F20	200 kV				

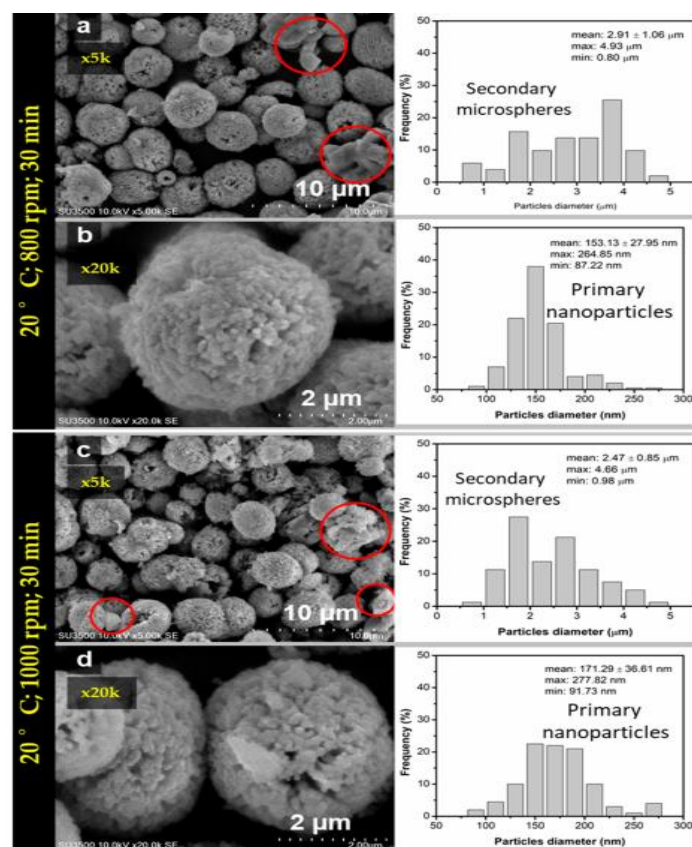


Figure 3 SEM image and vaterite particle size distribution (Figures were adopted from Febrida et al., 2021)

TEM analysis in Figures 4(a-d) also confirmed the morphology of the vaterite microstructure synthesized by the simple solution method. TEM images reveal CaCO₃ microspheres composed of many agglomerated nano-sized primary particles of relatively homogeneous size around 150 nm (Febrida et al., 2021).

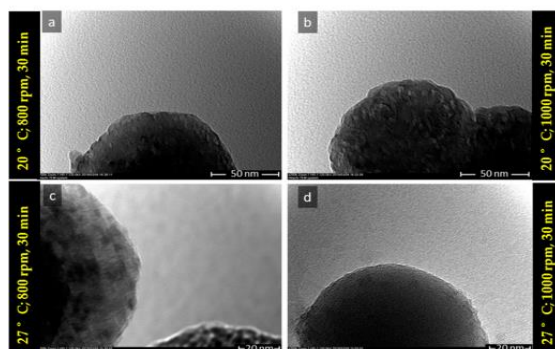


Figure 4 TEM image of vaterite (Figures were adopted from Febrida et al., 2021)

SEM and TEM images are showing the detailed morphology and inner structure of the spherical-structured CaCO_3 sorbent series. From Figure 5, the four sorbents appear to form a spherical structure in uniform size. The average diameter of CaCO_3 sorbents ($\text{Ca}_{30}\text{Mn}_1$, $\text{Ca}_{12}\text{Mn}_1$, and Ca_7Mn_1) were about 990, 1100, 1200, and 1300 nm, respectively. The diameter of the microspheres of all these sorbents is about 1 μm , therefore decreasing the Ca/Mn molar ratio can increase the diameter of the microspheres, although only slightly. From Figure 5(a), the CaCO_3 sorbent shell consists of loosely packed CaCO_3 nanoparticles with visible large macropores. Moreover, in the cross-sectional view of the CaCO_3 sorbent in Figure 5(a), it was seen that there were broken microspheres, indicating that the structure of the sorbent obtained without Mn doping was unstable. However, for the sorbents doped with Mn, namely the sorbents $\text{Ca}_{30}\text{Mn}_1$, $\text{Ca}_{12}\text{Mn}_1$, and Ca_7Mn_1 , from Figures 5 (d), (g), and (j), the shells of these three sorbents were all compact without fragments, indicating that doping with Mn gave the sorbent with a more stable structure to improve the stability of the absorption performance. From the TEM image in Figure 5, the three Mn-doped CaCO_3 -based sorbents have a double-shelled hollow microsphere structure, whereas fragments and double-shelled hollow microspheres can be found simultaneously in the TEM image of the pure CaCO_3 sorbent (S. Li et al., 2019).

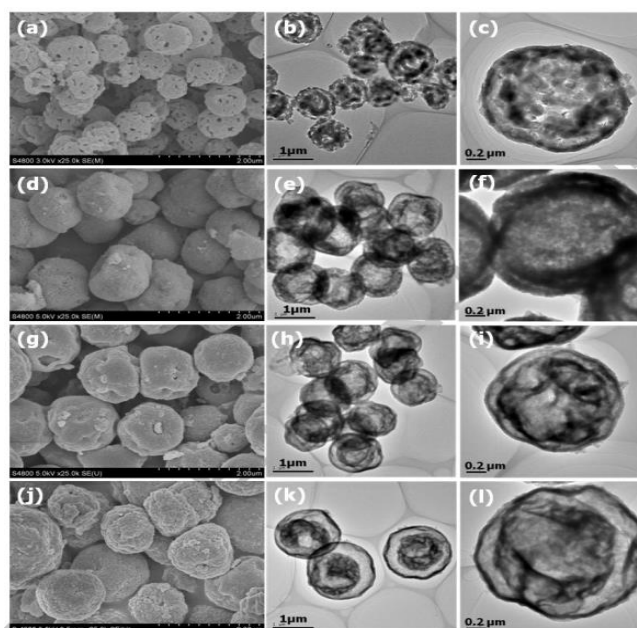


Figure 5 SEM and TEM images of double-shelled hollow microspheres with different Ca/Mn molar ratios; (a) SEM and (b, c) TEM images of pure CaCO_3 ; (d) SEM and (e, f) TEM images of $\text{Ca}_{30}\text{Mn}_1$; (g) SEM and (h, i) TEM of $\text{Ca}_{12}\text{Mn}_1$; (j) SEM and (k, l) TEM images of Ca_7Mn_1 (Figures were adopted from S. Li et al., 2019).

The size and morphology of CaCO_3 particles with mixed spherical and cubic structures (based on Zhang et al., (2018)) were also visualized through SEM and HR-TEM. As shown in the low-magnification SEM image (Figure 6(a)), the particle size of the synthesized CaCO_3 was between 2 and 10 μm and most of the particles were spherical, however, some particles were observed to have a cubic shape. The mixture of spherical and cubic particles shows a mixture of CaCO_3 polymorphs obtained into vaterite and calcite. Figure 6(b) shows a high magnification SEM image and the rough surface of the CaCO_3 particles can be seen from this image. The rough surface of the CaCO_3 particles shows a high surface area and the potential for pores. The dark center and pale edges which are visible under TEM, further indicate the porous nature of the particles (Figure 6(c)). HRTEM also confirmed the rough and porous nature of the surface of those CaCO_3 particles, and the particles were composed of fused nanoparticles, explaining the roughness seen under TEM (Figure 6(d)) (Zhang et al., 2018).

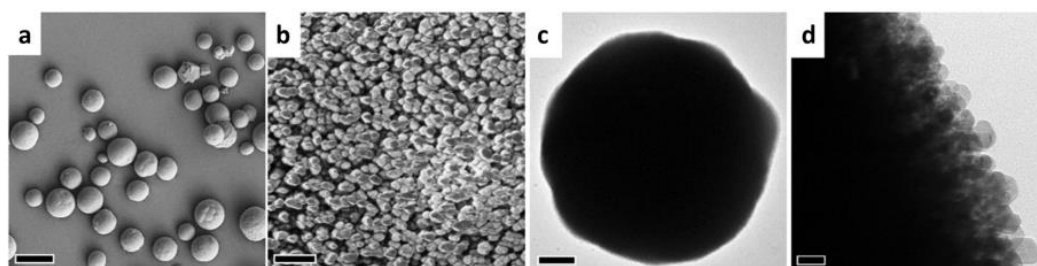


Figure 6 SEM (a and b) and TEM (c and d) Images of CaCO_3 microparticles (Figures were adopted from Zhang et al., 2018).

L. Li et al. (2020) synthesized CaCO_3 composites of Gelatin- CaCO_3 . The morphology of CaCO_3 without addition also had a cubic-like granule shape and became more irregular after calcination. The synthesized CaCO_3 was in the form of microspheres, whose surface was getting smoother, and showed higher porosity on calcination. The surface morphology of the gelatin- CaCO_3 composite microspheres changed before and after calcination, as shown in Figure 7. In Figures 7(a1) and (a2), the gelatin- CaCO_3 microspheres are relatively compact with a diameter of about 3 μm , consisting of many small nanoparticles. After calcining at 550 $^{\circ}\text{C}$ for 2 h, abundant macropore structures on the interior and surface of the CaCO_3 microspheres were observed as shown in Figures 7(b1) and (b2). Interestingly, the diameter of the porous CaCO_3 microspheres was slightly larger than that of the gelatin- CaCO_3 microspheres. HRTEM image of gelatin- CaCO_3 microspheres shows a typical polycrystalline structure as shown in Figure 7(a3) where several amorphous regions correspond to significant gelatin. In addition, the interplanar distances were measured to be 0.275 and 0.249 nm, corresponding to the (114) vaterite plane and (110) calcite plane. HRTEM image of porous CaCO_3 microspheres (Figure 7(b3)) after calcination shows a typical single-crystal diffraction point, the interplanar distance is 0.247 nm corresponding to the (110) calcite plane. Selected Area Electron Diffraction (SAED) pattern in Figures 7(a4) and (b4) confirms the transformation from vaterite to calcite after calcination. Therefore, the gelatin- CaCO_3 composite microspheres were a mixture of vaterite and calcite CaCO_3 , while the porous CaCO_3 microspheres after calcination were pure calcite, which indicated that crystal transformation occurred during the heating process (L. Li et al., 2020).

In addition, CaCO_3 was also found to have a chain/spheroidal structure studied by Kezuka et.al. (2018). Figures 8(a-b) show low magnified Bright Field (BF) TEM images of chain-like and spheroidal CaCO_3 particles. The average length and width of the chain-like particles were 152.3 nm and 34.7 nm, and the mean aspect ratio was estimated to be ~ 4.3 via TEM image analysis. The insert in Figure 8(a) shows the SAED pattern along the zone axis $[1\bar{1}00]$ of the region marked by the dotted circle. The dot separation cannot be seen in the SAED pattern. Therefore, neighboring crystallites are assumed to be mono-oriented concerning each other and each of these chain-like particles is a single crystal. In addition, the elongation direction of the chain-like particles was also found to be parallel to the c-axis of the calcite structure. This

direction corresponds to the elongation direction of the calcium carbonate single-crystal nano bars formed by the 1D-oriented attachment of the nano blocks. Figure 8(d) depicts a High-Resolution TEM (HRTEM) image of the chain-like particles from the dotted square region of Figure 8(c). The horizontal lines in the HRTEM images correspond to the dipolar planes of calcite (0001) and neighboring crystallites bonded at the atomic level. Moreover, the existence of narrowed knots between the crystallites can be confirmed (Kezuka et al., 2018).

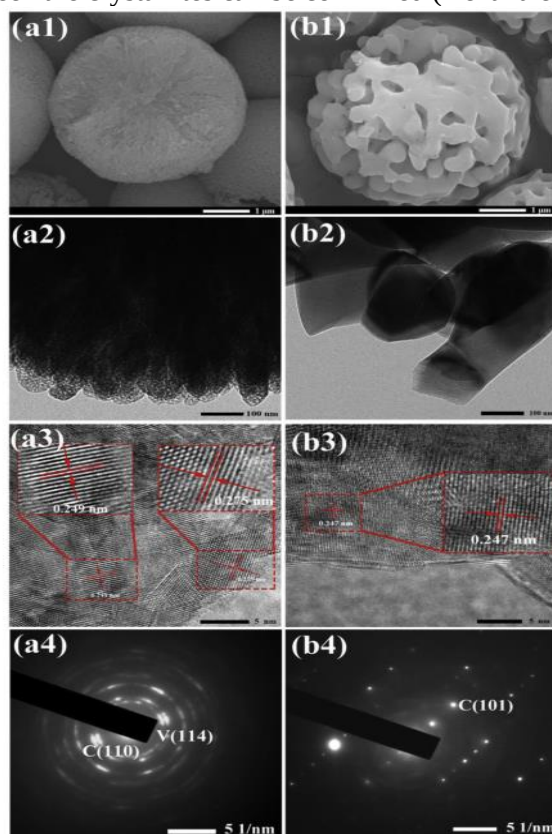


Figure 7 SEM and TEM Images of (a1, a2, a3) Gelatin-CaCO₃ Composite Microspheres; (b1, b2, b3) Porous CaCO₃ Microspheres; (a4, b4) SAED Pattern (Figures were adopted from L. Li et al., 2020)

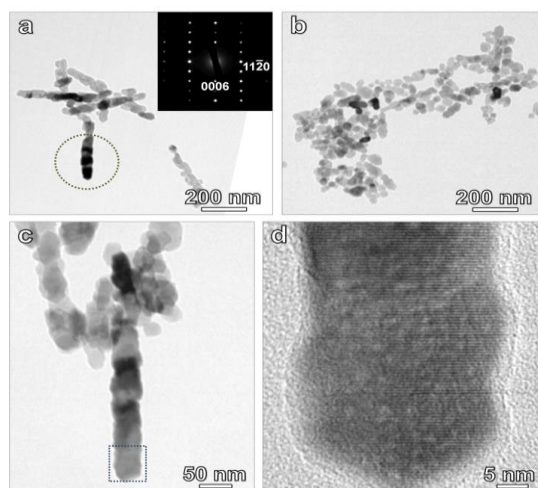


Figure 8 Chain and Spheroidal Primary Particle TEM Image (Figures were from Kezuka et al., 2018)

Figures 9(a-b) show typical FE-SEM images of the agglomerates of both types of particles synthesized with and without the addition of lime milk. The chain-like particles become entangled with each other to form fine clumps with sporadic pores. In contrast, spheroidal particles are denser without large pores in the agglomerates. The mean agglomerate size and agglomerate size at 10%, 50%, and 90% of the cumulative size distribution (D10, D50, and D90) were 2.3, respectively; 4.3; and 9.8 μm for chain-like particles and 1.9; 3.5; and 7.1 μm for spheroidal particles. It was quantitatively shown that chain-like particles form larger agglomerates than spherical particles. Figures 9(c-d) show cryo-SEM images of aqueous slurries of chain-like and spheroidal particles. The darker background matches the amorphous ice. In both images, most of the particles are from irregular agglomerates, although a few single particles can be observed. It was qualitatively observed that the chain-like particles formed larger agglomerates in the slurry (Kezuka et al., 2018).

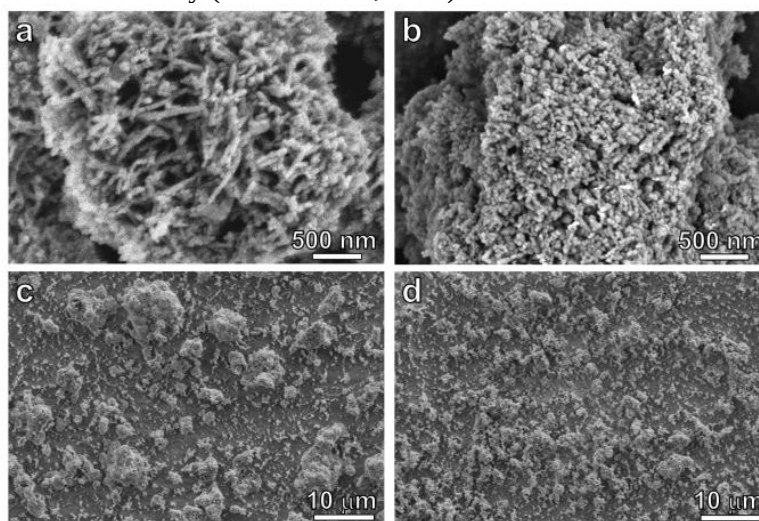


Figure 9 FE-SEM images of (a) Chain-like agglomerates and (b) Spherical particles. Cryo-SEM Images of (c) Chain-like aqueous slurries and (b) Spherical particles (Figures were adopted from Kezuka et al., 2018).

CONCLUSION

Based on the results of the search and investigation of literature studies that have been carried out, the SEM and TEM electron microscopy methods are indeed effective and very useful for characterizing the structure of CaCO_3 so that the design criteria for this CaCO_3 application can be designed better. From this study, most of the morphological forms of pure CaCO_3 are known to be spherical and some of them are cubic, in addition, there is also CaCO_3 which has a chain-like particle morphology. The crystalline form of CaCO_3 synthesized can also be identified through its particle morphology seen in SEM and TEM images.

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