

Marine Calcium Hydroxyapatite as Embryonic Material for Excellent Performance of Perovskite Solar Cell

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ABSTRACT

Marine calcium hydroxyapatite (HAp) extracted from fish bone has been perceived to be good as it carries good bioactivity and biocompatibility. In fact, the production of HAp from synthetic process involves many chemicals and complicated procedures which affect the stability. Extraction process of HAp from Selayang fish bone started with boiling fish bones to eliminate adherent fish meats, drying process and grinding process to obtain the powder. The extracted calcium was further used in synthesis of calcium titanate perovskite (CaTiO_3) for solar cell application. CaTiO_3 has been known as a material with high efficiency and smaller band gap which fulfill the requirements for fabrication of the solar cell. The perovskite were synthesized in various ratios to observe the stability and coequal character with the standard perovskite. The novelty of this study lies between the method of extraction of HAp and the fabrication of perovskite where the calcium is substituted with HAp. The obtained HAp and CaTiO_3 were characterized by using TGA, XRD and FTIR. The analytical results shows that HAp were formed after the calcinations process at 900°C and crystalinity of CaTiO_3 was found at XRD peaks 47.8°, 48.2° and 68.5°. Highest efficiency was measured at sample H_1T_1 perovskite with 5.3%.

Keywords: Calcium Titanate, Hydroxyapatite, Perovskite, Solar Cell.

1 INTRODUCTION

One of the most essentially detached of the environment conservation is to recycle discarded items in order to preserve the environment. Marine abduction contributes to more than 70% in the food processing industry and almost 30 million tons of fish byproduct has been junked including the non targetted species. As a result, every year considerable amount of the total catch is discarded as processing leftovers and that includes trimmings, fins, frames, heads, skin and viscera [1].

Thus, there is extraordinary potential in marine industry to disciple and use a greater amount of these byproducts as profitable materials. To deflate over exploitation inclusive of unfavorable environmental impacts, it would be prudent to go for acquiring of materials with high added value to be fabricated from rest-crude material.

Recent studies have identified a number of bioactive compounds from remaining fish muscle, collagen and gelatin, fish oil, fish bone, internal organs and shellfish [2]. This compound can be extricated and purified with advancement of technologies differing from elementary to complex processing. In this way, improvement of new innovations in order to produce novel compound

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from marine byproduct will bring more advantage and help in solving difficulties in recycling the discarded items. Fish bone byproducts known as hydroxyapatite (HAp) is considered as a potential source to obtain calcium since the structure is similar to calcium synthetic. HAp derived from fish bone that have a stoichiometric formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ show excellent bioactivity and more dynamic response to the environment than the synthetic HAp [3]. HAp from fish bone presents the advantage to preserve some properties of the precursor materials such as chemical composition and structure [4]. Hence, it is expected that biological HAp leads to better results as coating material when the properties are preserved [5]. Other studies reported the- use of fish bone from cephalopoda to obtain calcium phosphate via hydrothermal transformation [6]. This study presents a simple and modest technique to extract HAp from selayang fish bone via mechanochemical treatment and the application of HAp in the production of CaTiO_3 perovskite for solar cell application.

Photovoltaic (PV) technology has been established as one of the best solutions to bring forth flexible and long term solutions for electrification [7]. The future perovskite solar cell has prompted an adjustment in the worldview of developing photovoltaic innovation inferable from the huge increment in their power conversion efficiency. Proper understanding of the thin film deposition processes can help in achieving high efficiency device over large areas [8]. Perovskite which originated from CaTiO_3 is a general name for oxides having the structural formula ABO_3 . In the structure, A will be a bigger cation situated on the edge of the structure and B is a smaller cation located in the focal point of the octahedron. From the composition, it can be seen that perovskite oxides are compounds comprising at least two simple oxides having high melting points. CaTiO_3 has been subjected to the study because it is one of the few minerals that can be found in nature. Particularly, perovskite has a great potential in photocatalyst of organic pollutant degradation reaction because of its low cost, easy fabrication and high biocompatibility [9]. Mixed oxide perovskite containing calcium has regularly been expressed as base solid catalysts that show high catalytic activities. Futhermore, this material is a ferroelectric ceramic with perovskite related structure [10]. Titanium oxide thin films are expected to serve as a stepping stone for dielectric materials along with the utilization of CaTiO_3 in solar cell application. In order to make the HAp a reliable material in the fabrication of perovskite, mechanochemical treatment was introduced to extract the HAp from fish bone. The use of marine HAp can diminish the problems produced by HAp powder from synthetic processes which need additional chemical to improve the mechanical strength and many chemicals are involved in this process. Hence, the aim of this study is to extract HAp and synthesis CaTiO_3 perovskite by replacing calcium with HAp. HAp will take place at the A site cation owing to its long term characteristic as the cheapest source of calcium.

2. MATERIALS AND METHODOLOGY

2.1 Extraction of Hydroxyapatite From Fish Bones

Fish bone waste was obtained from the local fish cracker warehouse production. The species used for this study was Selayang which was abundant and can be easily obtained. Fish bone was segregate from the surplus meat through the bubbling procedure for a few hours to guarantee the expulsion of undesired debris stuck to it. Thereafter, the bones were washed thoroughly with tap water and dried at room temperature to make sure there is no water and organic portion left behind. Subsequently the crushing process takes place to reduce the size of the fish bone before it undergoes calcinations process at 900°C for 5 hours to attain raw hydroxyapatite (HAp). The calcined fish bones were milled for 2 hours at 200rpm under atmospheric condition in a planetary ball mill with one steel pot of 50cm^3 inner volumes and seven balls. Figure 1. below shows the overall process to extract HAp powder from the fish bone by product.

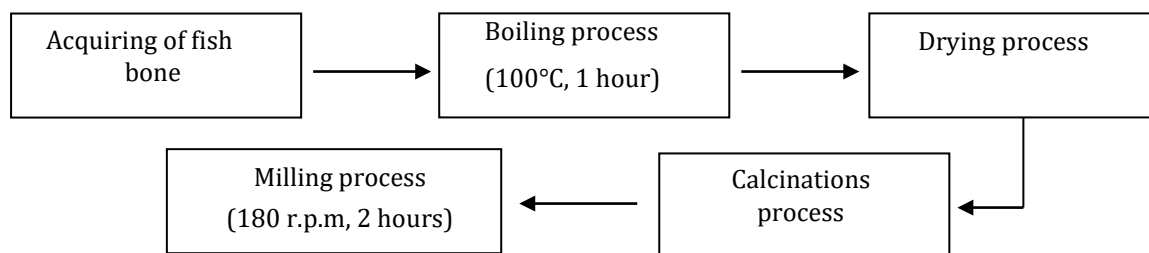


Figure 1. Flowchart of the overall process to obtain HAp.

2.2 Synthesis of Calcium Titanate (CaTiO₃) Perovskite from HAp and Titanium (TiO₂)

The CaTiO₃ perovskite was synthesized by using HAp and TiO₂ as the starting material. HAp was dissolved ultrasonically in 100ml deionized water for 30 minutes and simultaneously added to TiO₂. The process took a couple of hours to allow the reaction to fully take place in the mixture. The mixtures were then washed for a few times to remove the unreactive ions before it was brought into the drying process at 80°C for 24hours. The process to synthesize CaTiO₃ perovskite was performed by varying the ratio of HAp and TiO₂ as shown in Table 1 via mechanochemical treatment under milling condition. In mechanochemical synthesis of CaTiO₃, the starting materials will initially undergo structural defects and will be followed by a chemical reaction [11].

Table 1 Ratio of HAp to TiO₂ to synthesis CaTiO₃

Hydroxyapatite	Titanium Dioxide
1	1
1	3
1	5
1	7
3	1
5	1
7	1

2.3 Fabrication of CaTiO₃ on Fluorine Tin Oxide

CaTiO₃ obtained from various ratio of HAp and TiO₂ were coated on FTO thin films. The thin films need to undergo a cleaning process to avoid any contamination. The process was done as reported by a previous study [7]. First, the FTO must be immersed in the detergent solution for 10 minutes at 30°C followed by boiling in distilled water for 5 minutes at the same temperature. This step was repeated to ensure the FTO was free from the remaining detergent. After a thorough cleaning process of the FTO, the CaTiO₃ was pasted onto the FTO and then annealed at 120°C before undergoing further characterization.

2.4 Characterization of HAp and CaTiO₃

In an effort to synthesize CaTiO₃ from HAp and TiO₂, few analysis were conducted under few a conditions to make sure the product obtained was complementary with the standard perovskite form. Hence, the Thermal gravimetric (TG) analysis was carried out to study the thermal behavior of the HAp powder at the temperature range of between 0° to 900°C and the heating rate in nitrogen atmosphere. Fourier Transform Infrared (FTIR) spectrometer was used to analyze the functional group of HAp powder and CaTiO₃ in the range of 400-4000cm⁻¹. Xray

Diffraction (XRD) spectrometer was used to confirm the phase present in the HAp and CaTiO_3 . The behavior and reaction in both phases were studied from 10° to 80° XRD spectra with the step size of 0.1° . Electrical conductivity was done by using the four point probe and Electrical Impedance Spectroscopy was used to measure the power conversion efficiency of the solar cell.

3. RESULTS AND DISCUSSION

3.1 Thermal Gravimetric Analysis (TG) of HAp

TG analysis has been used to observe thermal behavior and the weight loss of HAp based on thermoanalytical curves. This analysis was the main key to confirm the optimum temperature to obtain pure HAp. The first weight loss in Figure 2. was observed at endothermic peak at temperature less than 100°C with the rapid mass loss which gives 9.12% corresponding to 3.15mg of HAp. This loss is due to adsorbed water [12]. The weight loss that took place at 150° - 200° might be attributed to the partial crystallization of HAp losing some lattice water simultaneously. The next loss in fish bone is observed at 360°C which is assigned to the decomposition of organic compounds. Increasing temperature up to 600°C was assumed to be result in gradual dehydroxylin of hydroxyapatite [13]. The decomposition at a later stage was related to the decarbonization of CaCO_3 to form CaO [14, 15]. Equation 1 shows HAp loss quantity from 900°C and above corresponding to every HAp molecule losing one molecule of H_2O [16]. From the TG curve in Figure 2, it can be confirmed that the temperature needed for the calcinations process to obtain pure HAp is 900° which indicates the high thermal stability of the sample which is also supported by other studies [17, 18].

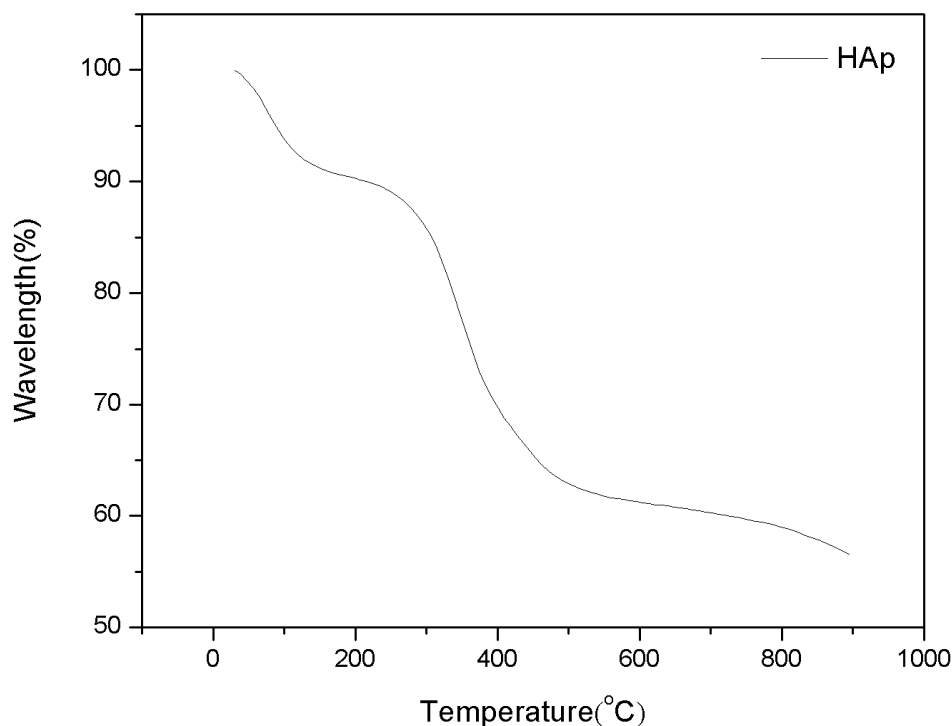


Figure 2. Thermal gravimetric analysis of HAp.

3.2 Fourier Transform Infrared Spectroscopy of HAp and CaTiO₃

FTIR study was carried out to deliberate the functional group present in CaTiO₃. To confirm the reaction between HAp and TiO₂ in the formation of CaTiO₃, Figure 2. shows the FTIR spectra for HAp before and after the calcinations process to obtain pure calcium while Fig. 3 shows the spectra of the CaTiO₃ form from the reaction between the extracted HAp and TiO₂ in the range of 400 to 4000 cm⁻¹. The FTIR shows a rough spectra in raw HAp at 3000 to 3700 cm⁻¹ before calcination which corresponds with the OH⁻¹ stretching of H₂O. The bands around 1635-1648 cm⁻¹ attribute to amide I, II and III bands found in raw fish bone [19]. However, these functional groups are lost during the calcinations process. The bending mode of the B-type carbonate HAp can be consigned at peak 858 cm⁻¹ [20]. In the band between 579cm⁻¹ and 607cm⁻¹, it shows the characteristic peaks of PO₄³⁻ bending mode [5, 21]. The crystalline phase was revealed due to the large parting bands distance of the starching and bending mode PO₄³⁻ at peak 1016cm⁻¹ and 568cm⁻¹ respectively. Due to the substitution of PO₄³⁻ by CO₃²⁻ after the calcination process, the peak at 1427cm⁻¹ is associated with the bending B-type carbonate. The FTIR pattern confirms that the extract powders are HAp powders and follow the same pattern as the synthetic HAp [22].

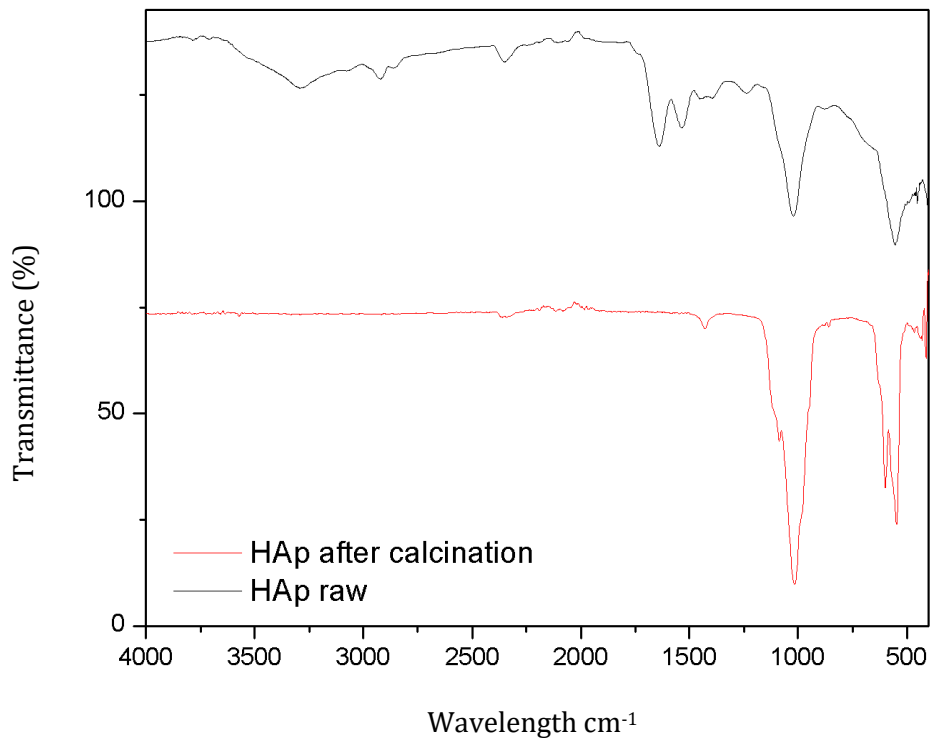


Figure 3. FTIR spectra of HAp before and after calcinations to obtain pure calcium.

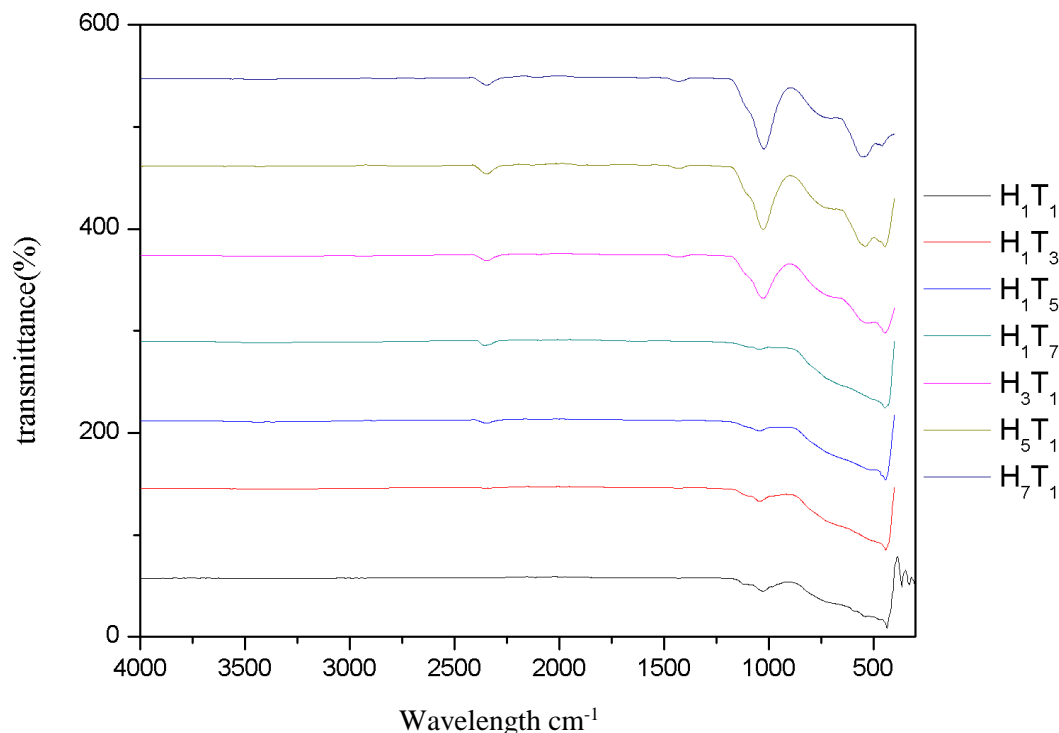


Figure 4. FTIR spectra from reaction of HAp and TiO_2 to form CaTiO_3 .

In distinction to Figure 4, H_1T_1 spectra at 1000 to 1190cm^{-1} were related to Ti-O bond while the characteristic peaks for CaTiO_3 was detected at 590cm^{-1} which confirm the reaction between HAp and TiO_2 . The ideal cubic structure was found at 457cm^{-1} and by observing the FTIR element in H_3T_1 , H_5T_1 and H_7T_1 it shows the lower peak of TiO_2 after escalation of HAp whilst the establishment of CaTiO_3 was sharpened from H_3T_1 to H_7T_1 . Per contra, in H_1T_3 , H_1T_5 and H_1T_7 with increasing TiO_2 , the amount of PO_4^{3-} was dwindling resulting in acuminate of Ti-O bond at 1130cm^{-1} . The keen traces in FTIR from Figure 3 and 4 demonstrate the presence of the occupancy of the functional group which were PO_4^{3-} , Ti-O and CaTiO_3 can be proved. The absence of OH was related to high the calcination process.

3.3 Xray Diffraction Spectrometer (XRD) of HAp and CaTiO_3

XRD analysis was done to support the data from the FTIR. The purity and stability of HAp and CaTiO_3 perovskite were analysed via XRD. Figure 5. shows small peaks characteristic resolve at 2θ value along at 25° , 30° , 40° and 50° in the extracted HAp. Low and rough peak in HAp before the calcination process indicated the weak crystallization of raw HAp powder. In contrast, HAp after the calcination process shows clear and sharp peaks which explains the increasing crystallization of HAp due to the heat treatment. The pinnacles of intensity increased with the augmentation of the calcination temperature. This is due to the expulsion of organic portion and substances in the HAp powder [23]. CaO and $\text{Ca}(\text{OH})_2$ were found at 50° , however when CaO reacted with water molecules, alkaline calcium hydroxide formed hence acknowledged as impurity. The peak broadness was due to either smaller crystallite sizes or the amorphous nature of materials. The issue of phase stability in CaTiO_3 derived from marine calcium and TiO_2 is shown in Figure 6. Major characteristic peaks of CaTiO_3 were present at 47.8° , 48.2° and 68.5° (PDF card No. 75-2100, XRD library) in the sample obtained from the reciprocation of HAp and TiO_2 .

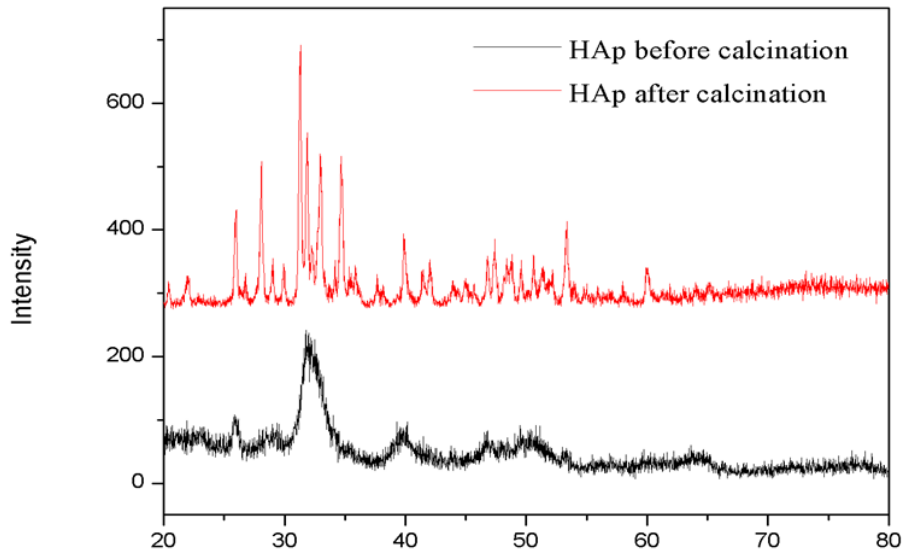


Figure 5. XRD pattern of HAp before and after calcinations.

For sample H_1T_1 , the content of HAp and TiO_2 were relatively equivalent. It was shown that TiO_2 was pure anatase at 24.9° [24] while at the same time, the main characteristic diffraction peak of $CaTiO_3$ appeared at 47.8° which documented the consequent associated phases of HAp and TiO_2 . This phase characteristic also appears in other samples (Figure 6) but however there were significant difference between the peak with a constant amount of HAp and a constant amount of TiO_2 . When the amount of HAp was fixed for the sample H_1T_3 , H_1T_5 , and H_1T_7 , it could be clearly seen that the patterns for H_1T_3 and H_1T_5 , were almost similar and there was an overlapping of TiO_2 and $CaTiO_3$. Likewise, the characteristic peaks for the fixed amount of TiO_2 shows instability of phase crystallization of $CaTiO_3$ due to high HAp content. The presence of β -tricalcium phosphate was detected to a weaker developed perovskite due to the partial dissociation of HAp [25]. Rough and low peak of $CaTiO_3$ were detected in H_3T_1 , H_5T_1 and H_7T_1 .

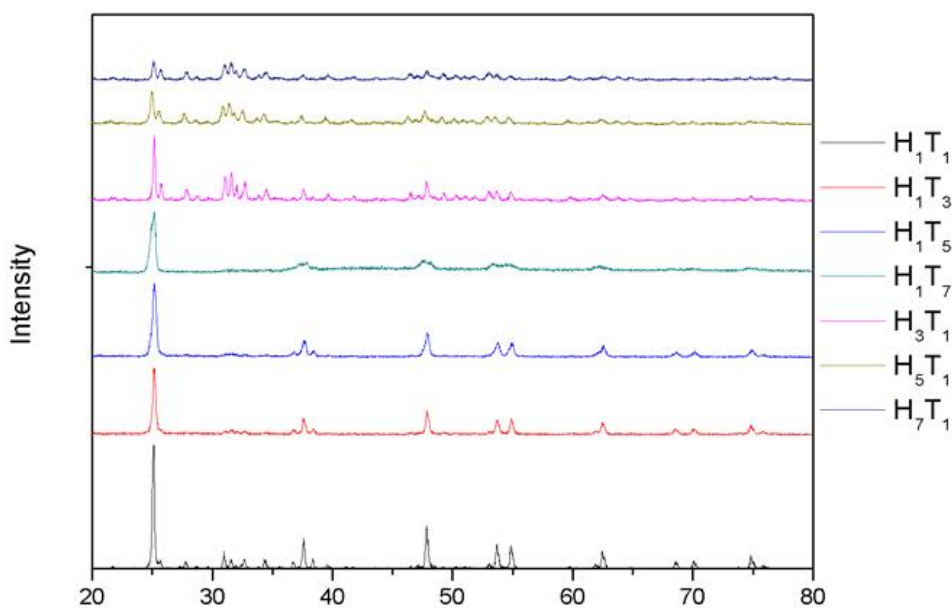


Figure 6. XRD pattern for variance ratio of HAp and TiO_2 .

3.4 Electrical Conductivity Measurement

The ability to convey a current in a material is known as electrical conductivity. The current is conveyed by ions and the chemical charges that occur in the material. Conductivity is an inherent property of a material which is also known as specific conductance. Figure 7. shows the electrical conductivity of a single layer of CaTiO_3 synthesized from HAp and TiO_2 . H_1T_1 CaTiO_3 perovskite to give the highest electrical conductivity with 1.37 S/cm followed by H_7T_1 , H_1T_5 , H_1T_3 , H_5T_1 , H_3T_1 and H_1T_7 .

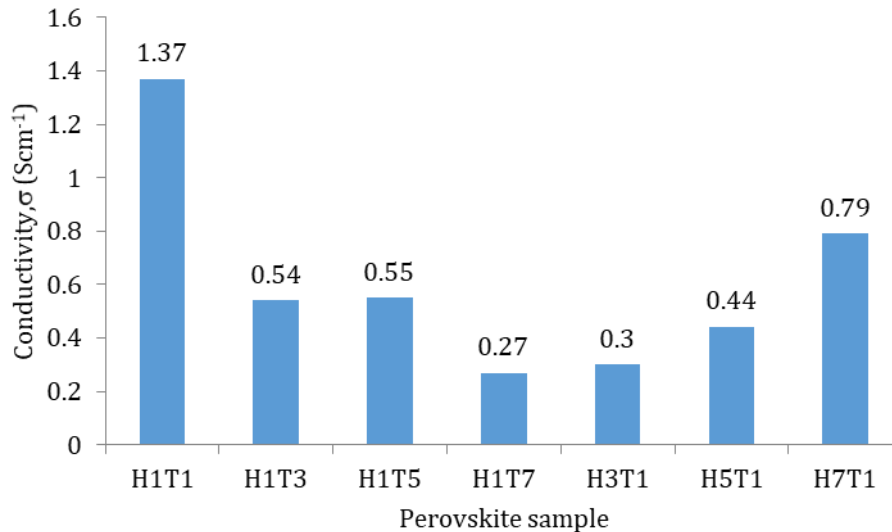


Figure 7. Electrical Conductivity of variance ratio of CaTiO_3 perovskite from reaction of HAp and TiO_2 .

3.5 Power Conversion Efficiency

Higher power conversion efficiency (PCE) of solar cells is defined as solar cells with optimum performance. However, PCE is strictly dependent on the device parameter that can be observed from I-V curve. I-V characteristic of each samples provide information such as maximum power (P_{max}), maximum current (I_{max}), maximum voltage (V_{max}), fill factor (FF), short circuit current (I_{sc}) and open circuit voltage (V_{oc}) which give a huge impact on the performance of PCE of solar cells. P_{max} was calculated by multiplying I_{max} to V_{max} obtained from I-V curve. FF determines the quality of the curve and it depends on the ratio between I_{sc} , V_{oc} , I_{max} and P_{max} . FF is not only dependent on the mobility (μ)-lifetime (τ) product of the bulk materials but also on the thickness of the active layer and the morphology of interface between cathode/active layer [26]. FF can be related with current and voltage as :

$$FF = \frac{(I_{\text{max}})(V_{\text{max}})}{(I_{\text{sc}})(V_{\text{oc}})} \quad (2)$$

Solar cells that have high ability to convert absorbed light into electrical energy is considered as high efficiency solar cells. PCE of the cells can be calculated by using formula:

$$PCE = \frac{(I_{\text{sc}})(V_{\text{oc}})(FF)}{P_{\text{in}}} \quad (3)$$

Table 2 Power conversion efficiency of different ratio HAp and TiO₂ in formation of CaTiO₃

	I_{max} (x10⁻⁶A)	V_{max} (x10⁻¹V)	I_{sc} (x10⁻⁶A)	V_{oc} (x10⁻¹V)	P_{max} (x10⁻⁷W)	P_{in} (x10⁻⁵W)	Eff (%)	FF (x10⁻¹)
H₁T₁	-3.36	2.36	-6.42	4.67	-7.93	1.5	5.3	2.6
H₁T₃	-1.08	1.95	-2.07	3.77	-2.10	1.5	1.4	2.7
H₁T₅	-6.43	1.55	-1.28	3.20	-1.00	1.5	0.7	2.4
H₁T₇	-3.95	1.45	-6.75	2.86	-5.70	1.5	0.4	3.0
H₃T₁	-3.75	1.95	-7.30	3.97	-7.30	1.5	0.5	2.4
H₅T₁	-2.06	2.06	-4.02	3.97	-4.20	1.5	2.9	2.7
H₇T₁	-1.54	2.86	-2.87	5.18	-4.40	1.5	2.9	3.0

Figure 8 shows perovskite with H₁T₁ showed the highest PCE with 5.3% compared to other ratios followed by samples H₅T₁, H₇T₁, H₁T₃, H₁T₅, H₃T₁ and H₁T₇. Low crystallization of CaTiO₃ perovskite of samples H₁T₅, H₁T₇ and H₃T₁ affected the percentage of PCE in perovskite solar cells.

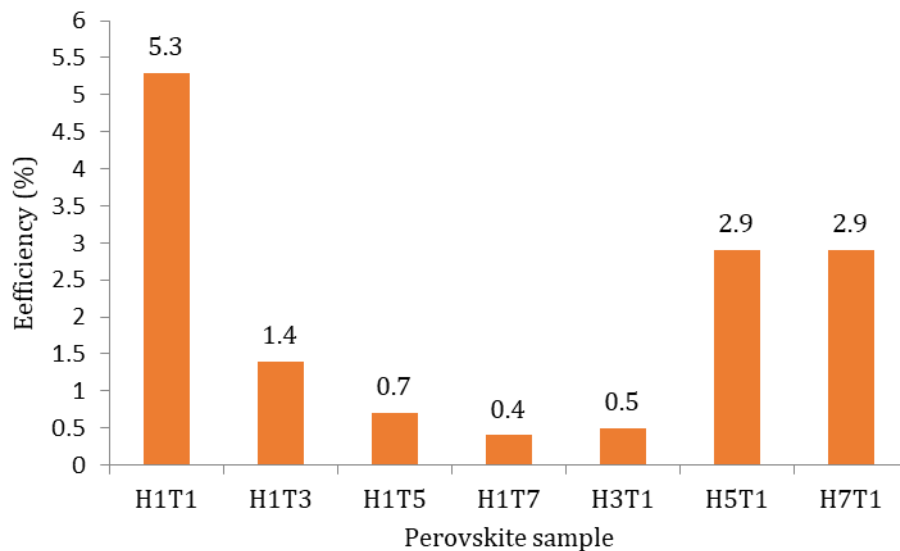


Figure 8. Excellent power conversion efficiency of different ratio CaTiO₃ perovskite.

4. CONCLUSION

Perovskite solar cell is a new type of PV device that serves as an excellent light absorbing and charge transporting characteristic. By continuous study and enhancing the architecture of the device, it is believed that this PV device can replace the conventional solar cell. Eventhough the perovskite solar cell has good efficiency, the commercialization of this device still needs to be studied. The solar energy is regarded as environmentally safe and clean. By using HAp from the fish bone by product, it indeed contributes in decreasing the amount of waste and pollution on earth. The performance of CaTiO₃ perovskite synthesize from HAp extracted from fish bone gives excellent power conversion efficiency which is 5.3%. Calcium from HAp should be considered a new potential material that is cheaper in price- compared to synthetic calcium. Furthermore, it can be found abundantly from discarded items of marine byproducts. Based on XRD analysis, the characteristic peaks of HAp and TiO₂ seem to disappear with the acute peak of CaTiO₃. The good biocompatibility of HAp used in the formation of CaTiO₃ which is known as a

good electric conductor contributes to the good performance of the perovskite solar cell.

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