

Development and Characterization of Calcium Oxide Nano-Particle from a Household Waste (Chicken Eggshell) in Mubi, Adamawa State Nigeria

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Abstract - CaO nanoparticle was synthesized from a chicken eggshell by the means of Chemical Co-precipitation of wet chemical synthesis method and this process basically be classified under the Bottom-Up process of production of nanoparticles. This shows the utilization and recycling of household wastes and the recycling process may also be performed on other household waste. XRF shows the total composition of 98.64%. This shows the perfection, precision and accuracy of the procedure utilized during the processes. The elemental composition shows that the Ca is with 56.65% and 43.35% oxygen. SEM analysis shows that the particle size is nearly cubic in shape and the approximate size of the particle was calculated using Debey Scherrer equation and found to be 23.76nm. The Energy Dispersive spectroscopy of the substance shows the highest optical dispersion of Ca at 3.5keV while oxygen shows optical dispersion at 0.50KeV. Thermo gravimetric analysis shows that the synthesized particle is thermally stable, 50% of the particle show perfect stability even at temperature of 950°C. FTIR analysis of the synthesized particle shows very limited signals on the absorption band and this clearly indicates the total conversion of the main components of eggshell (CaCO_3) into CaO nanoparticle.

Keywords - Calcium Oxide, Nano-Particle , Household Waste, Chicken Eggshell.

I. INTRODUCTION

Eggshells are as mineral fillers in thermoplastic materials like high density polyethylene (HDPE). Natural source of carbonates as a filler material have been adopted widely enhancing the rigidity, thermal stability and density of plastic materials (Sutapun *et al.*, 2015). Most of the construction failures are attributed to poor strength of soil. Stabilization of soil by the addition of lime, cement, bitumen, etc. is quite expensive. Eggshells could be a profitable replacement improving not only physical but also mechanical properties of soil (Kumar *et al.*, 2014; Hossain *et al.*, 2014). Recently, the utilization of natural sources from waste materials, i.e. eggshells, has been considered as a new trend for biodiesel production (Buasri *et al.*, 2013). Investigations associated with the consumption of the

eggshell waste as a renewable catalyst has already been mesmerized. Using eggshell wastes as raw materials for catalyst synthesis is a lucrative approach indeed (Fernandes *et al.*, 2013). Extraction of the bioactive compounds present in the eggshells would be beneficial for cosmetic and pharmaceutical industries. Moreover, eggshells could serve as a valuable and sustainable resource for the raw materials to make glass, glass-ceramic or ceramic products. Therefore, the present work contemplates on the extraction and characterization of one of the most easily accessible as well as useful source of raw material from eggshells and evaluates its beneficial applications.

Food wastes are found to be the origin of several health and environmental hitches. According to the Food and Agriculture Organization (FAO) of the United Nations, the

worldwide direct economic cost of food waste was \$750 billion in 2013 (FAO, 2000). which is increasing tremendously. Almost all food wastes contain some sort of useful minerals. Hence, it is obligatory to find out an alternative route of valuable mineral extraction from these food wastes and overcome the high disposal costs and environmental concerns (Envir. Com. Report, 2010). However, for the utilization of these organic food wastes having energy, water and mineral content, proper disposal of these are mandatory. Government regulations concerning landfills can lead to an economic stimulus to create value out of these wastes (Lin *et al.*, 2013). Among the various food wastes, eggshells have many bioactive compounds exhibiting high economic values.

Eggshells are basically comprised of a network of protein fibers along with some mineral compounds like calcium carbonate, magnesium carbonate and calcium phosphate. A trace amount of sodium, potassium (K^+), zinc (Zn^{2+}), manganese (Mn^{2+}), iron (Fe^{2+}) and copper (Cu^{2+}) have also been reported previously. However, almost 94-96% of an eggshell is reported as $CaCO_3$ which is the major constituent of many manufacturing industries. A good quality eggshell might contain as high as 2.2-5.5 g of $CaCO_3$. Consumption of eggshell as an affluent source of $CaCO_3$ could solve both ecological and financial interest (Rahman *et al.*, 2014).

II. EXPERIMENTAL DESIGN

A. Materials

Eggshell, Nicolet IR 100 FTIR Spectrometer, X-Ray diffractometer (XRD), X-ray fluorescence (XRF), Deionized water, stirrer, measuring cylinder, reactor, weighing balance, oven etc. are the materials used. Some of the reagents to be used includes; distilled water, methanol, sodium hydroxide was obtained from the laboratory, Mpdiibo Adama University of Technology Yola, Adamawa state and American University Yola, Nigeria.

B. Sample location and collection

Egg shells were collected from the household waste and the local tea vendors in Mubi town, northern senatorial zone of Adamawa State of Nigeria, it was properly washed three times with tap water to remove the unwanted materials adhered on the surface and properly rinsed twice with distilled water, it was then dried under shade at room temperature.

C. Sample preservation

The sample was collected in a container and preserved according to the standard method of American Public Health (APHA).

D. Quality assurance

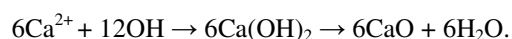
All reagents used were of pure analytical grades. Contamination was thoroughly checked by running a blank of all determinations. Glass apparatus used were soaked in a clean soap solution and in H_2SO_4/HNO_3 mixture and then rinsed with distilled water.

E. CaO Catalyst preparation

Highly active CaO was prepared by the calcinations-hydration-dehydration treatment of the eggshell. The dried eggshell was reduced to the smallest size and calcined in a muffle furnace under static condition at $900^\circ C$ for 5 hours, this is believed to transform the calcium species ie $CaCO_3$ and other substances in the eggshell into CaO and can be denoted as eggshell – CaO – 900 (Niju *et al.*, 2014)

F. Synthesis of CaO nanoparticles catalyst

A simple and cost effective synthetic route was adopted to synthesize inorganic metal oxide nanoparticle using thermal decomposition/chemical co-precipitation. In this process drop by drop addition of an aqueous sodium hydroxide (NaOH) in 20ml solution of a calcined chicken eggshell which resulted in the supersaturated aqueous solution of CaO, under vigorous stirring at $60^\circ C$ on a magnetic stirrer for 60 minutes. This forms a colloidal solution of calcium hydroxide ($Ca(OH)_2$). The obtained white colloidal solution of calcium hydroxide ($Ca(OH)_2$) was washed in an alcoholic suspension to remove sodium and enhance its stability due to a lower degree of agglomeration. The resulting suspension was passed across 125mm Whitman filter paper and dried at $60^\circ C$ in an oven for 4 hours. These nanoparticles were then stored in a desiccators box for use. The ionic equation of the reaction can be predicted to be as follows:



G. Catalyst characterization

The synthesized particle calcium oxide nanoparticle was characterized by;

- XRF to ascertain the chemical composition and the elemental composition of the particle and finally the optical dispersion of the components.

- SEM to look at the morphological being; their orientation, shape and to be able to calculate its approximate size.
- TGA Thermo-gravimetric analysis; this is a thermal analysis which shows the thermal stability of a substance.

H. Procedure for TG FT-IR determination

In the TG-FTIR experiment, Sample was placed in a ceramic crucible in a thermogravimetric analyzer (PerkinElmer, STA8000). The sample (33.350 mg) was heated from 30 °C to 1000 °C. The heating procedure goes as follows;

First, it was heated from 30 °C to 600 °C at once 20 °C/min. and was halt constantly at that 600 °C for 10 min. it was again heated from 600 °C to 700 °C at interval of 20 °C/min. and halt at 700 °C for 20 min. It was again heated from 700 °C to 800 °C at 20 °C/min. and halt for 10 min at that temperature i.e., 800 °C. And was lastly heated from 800 °C to 900 °C at 20 °C/min and was halt for 10 min. High-purity nitrogen was used as a carrier gas during the pyrolysis tests.

The evolved gas was carried by the carrier gas to the sample cell of FTIR spectrometer (Hyphenated Technology Compendium; PerkinElmer, Frontier) and then transferred to the injection port of a TG-FTIR system (PerkinElmer, STA8000). The FTIR sample cell temperature was kept at 900°C, and the resolution was set at 1 or 4 cm⁻¹. The scanning range was 450–4000 cm⁻¹. Time Base software was used to record the spectrum based on TG sample temperature. The gases evolved at selected temperatures were analyzed. The gas sample loop volume was 1 mL, and the injection time was 10 minits. Gas analysis was performed using FTIR. All transfer lines in the evolved gas analysis system (EGA PerkinElmer, TL9000) were maintained at 20 °C interval to avoid condensation of volatile gases with boiling temperatures less than 280 °C.

The transfer and source temperatures were 20 °C. Mass spectra were recorded in the mass range $m/z = 35 - 500$. Mass of the chicken eggshell keep depreciating from 33.4 mg to 17.50 mg. Analyte was identified based on the mass spectra shown as can be seen in the

- FTIR, this analysis was performed to see the functional groups present in the row eggshell and the synthesized particle.

III. RESULTS AND DISCURSION

A. X-ray Fluorescence (XRF) Spectroscopy Analysis

Quantitative analysis of the major minerals within the samples was done by X-ray Fluorescence Spectroscopy using a Magi X Pro XRF Spectrometer. For this purpose, a mass of 8/g of each of the powdered samples was mixed with 2 g of Herzog organic binder. The organic binder contained 90% cellulose and 10% wax. The mixture was further ground and homogenized using a mill. The homogenized samples were placed in an aluminum cup and hydraulically pressed into pellets under very high pressure of 20 tones for 60 seconds. This was done to ensure sample integrity under the vacuum and a consistent surface to receive the X-rays.

The CaO nanoparticles from egg shell was fully characterized (mineralogical and chemical compositions, particle size distribution, and so on) in this study.

Table 1. Chemical composition of CaO nanoparticles from egg shell.

Compounds	Conc. Units
CaO	98.64 %
Sc ₂ O ₃	0.30 %
V ₂ O ₅	0.03 %
Cr ₂ O ₃	0.01 %
SrO	0.03 %
CoO ₂	0.33 %
Pr ₂ O ₃	0.04 %
Eu ₂ O ₃	0.13 %
Tb ₄ O ₇	0.07 %
Dy ₂ O ₃	0.20 %
Tm ₂ O ₃	0.08 %
HfO ₂	0.07 %

Table 2. Elemental compositions of CaO nanoparticles.

Element	Weight (%)
Oxygen	43.35
Calcium	56.65
Total	100

Table 2. shows the elemental composition of CaO checked by XRF, it is clear that the dominant element in calcium oxide Nanoparticle is the Calcium which have the highest percentage of 56.65%, while the remaining percentage i.e. (43.35%) is Oxygen.

XRF data revealed the chemical and elemental compositions of the prepared CaO nanoparticles material from egg shell. Table 1 and Table 2 presents the compositional values obtained from the XRF analysis of the prepared/synthesized CaO nanoparticles from egg shell.

X-Ray Fluorescence (ED-XRF): This is for analyzing the elemental composition of the starting, intermediate and the final product. X-ray fluorescence is the emission of characteristic 'secondary' (or fluorescence) X-rays from a material that has been excited while bombarding with high energy X-rays or gamma rays.

XRF spectrometer operation was based on the emission of the excited elemental components of the sample Calcium Oxide nanoparticle through the bombardment of the sample with high energy X-rays.

In this study, the XRF results (Table 1.) revealed the highest content of CaO composition of 98.64%, followed by Sc_2O_3 with 0.30%, CoO_3 with 0.04%, Dy_2O_3 with 0.26%, Eu_2O with 0.13%, Tb_4O_7 with 0.074%, HfO_2 with 0.071%, Tm_2O_3 with 0.068%, Pr_2O_3 with composition of 0.04%, SrO with composition of 0.036, V_2O_5 with total composition of 0.03%, and Cr_2O_3 with total composition of 0.01% in the synthesized materials. Results reported by (Edeh *et al.*, 2018), also showed CaO as the highest content in a prepared catalyst system. Also another result from (Ayoola *et al.*, 2018) reported CaO nanoparticles as high as 99.230% and 96.131%, for nanoparticles from conventional CaO and uncalcined eggshell respectively. They also reported SrO as high as 0.120% and 0.305% for conventional CaO and uncalcined egg shell respectively whereas Pr_2O_3 0.040% was only found reported for conventional CaO. However, the XRD spectral analysis results thus support the XRF inferences.

In Table 2. the elemental composition of the synthesized Calcium Oxide from eggshell indicates that there is higher percentage of calcium with up to 56.65% while oxygen has the lowest percentage of 43.35. This equally indicates a high purity in comparison with the research/study reported and published by (Ayoola *et al.*, 2018).

B. Scanning Electron Microscope Materials

Back-scattered electrons imaging, quantitative X-ray analysis, and X-ray mapping of specimens often requires grinding and polishing the surfaces to an ultra-smooth surface. Specimens that undergoes Wavelength Dispersive X-ray Electron Spectroscopy (WDS and EDS). This is a method used to count the number of X-ray of the specific wavelength diffracted by crystals, analysis is often Carbon-Coated. In general, metals are not coated prior to imaging in the SEM because they are conductive and provide their own pathway to ground (Chandler *et al.*, 2009).

Fractography is the study of fractioned surfaces that can be done on light microscope or commonly on SEM. The fractured surface is cut to suitable size, cleaned of any organic residues and mounted on a specimen holder for viewing in the SEM (de Jonge and Rose, 2011).

Integrated circuits may be cut with a focused ion beam or other ion beam milling instrument for viewing in the SEM. The SEM in the first case may be incorporated in to the FIB. Metals, Geological specimens and integrated circuits all may also be chemically polished for viewing in the SEM. Special high resolution coating techniques are required for high-magnification imaging of inorganic thin films (Takaku *et al.*, 2015).

Figure 1 is the 15Kv image of calcium oxide nanoparticle of chicken eggshell viewed at 100um size. Waste eggshells were first carefully washed in clean water to remove sand, tissue, and other impurity present, dried in oven at 100 °C for 50min. The thin lining in the inner part of the shells were carefully removed.

SEM micrographs in Figure 2. have nearly cubic shapes of synthesized CaO nanoparticles with ~ 200nm average particle size on the cross-sections. Structural characterization through SEM was rather a direct way that provides visual demonstration to estimate particle size exactly. Typically, the SEM image of the synthesized CaO nanocrystals/ Bright field images of the sample indicate that the sample was dispersive single-crystal particles having cubic shapes.

Figure 3. is the 80um view of the synthesized calcium oxide nanoparticle from chicken eggshell. It is the 15KV image of the particle. At this size, it does not show the clear view of the nanoparticle size and structure but larger than the view at 100um.

C. Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy shows the presence of elemental calcium signal was confirmed in the sample (Figure 4.). The CaO nano-crystallites displays an optical absorption band peaking at 3.5keV while the second highest

optical absorbed is the oxygen which absorbs at 0.5keV which is typical of the absorption of metallic nano-crystallites of calcium and the oxygen respectively.

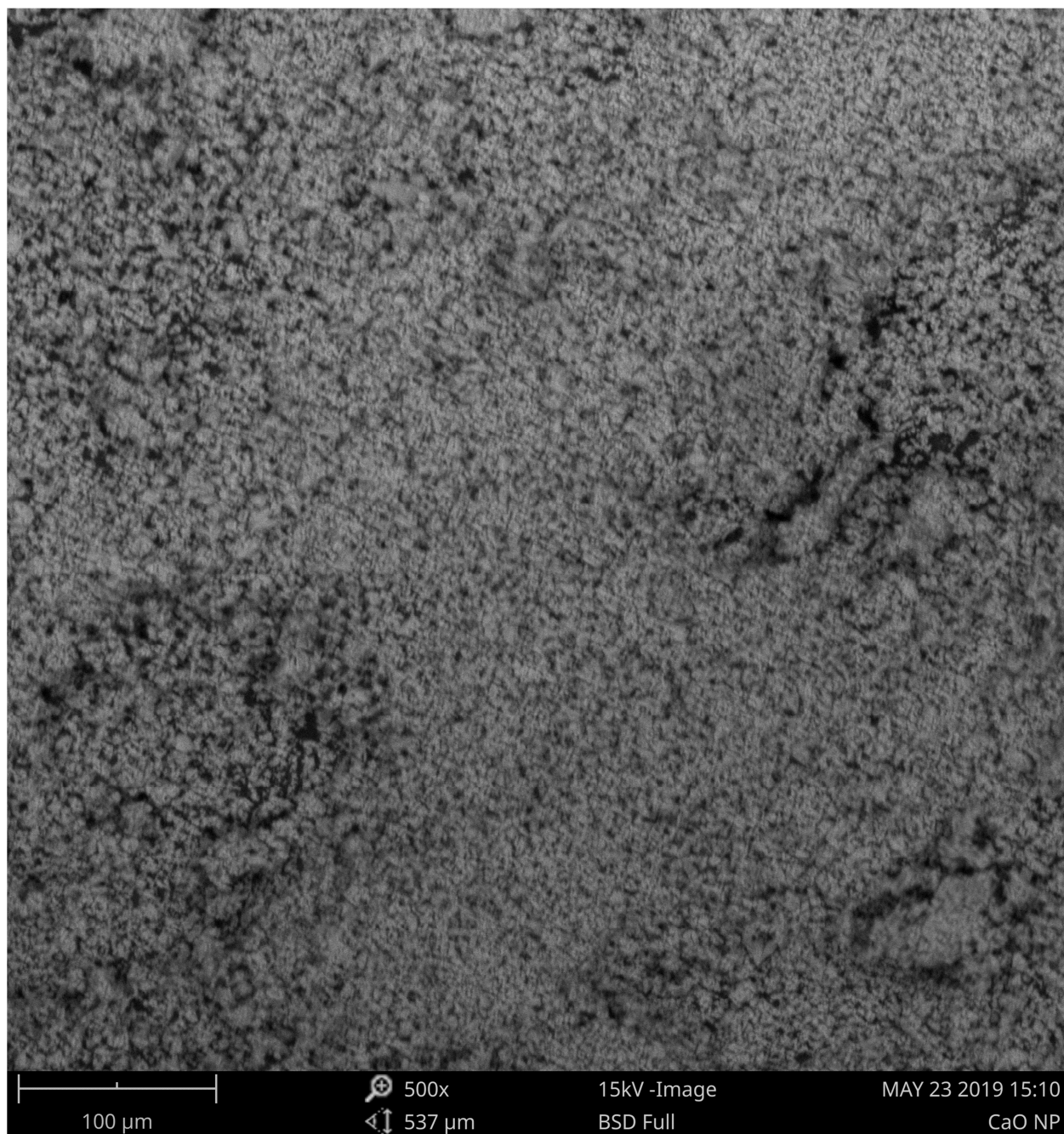


Figure 1. 100um 15kV-image of CaO nanoparticle.

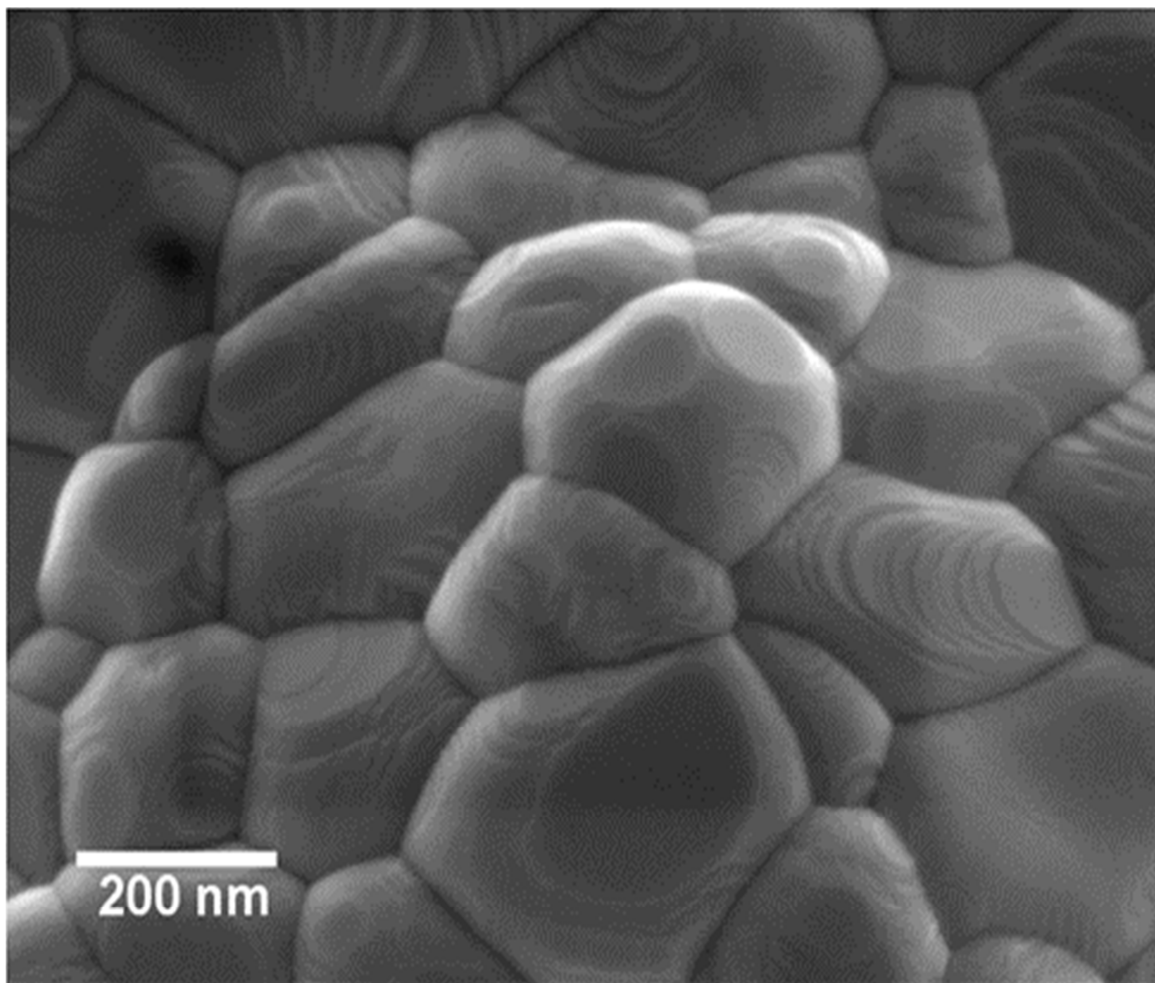


Figure 2. SEM Nanocrystal 200nm image of CaO Nanoparticle.

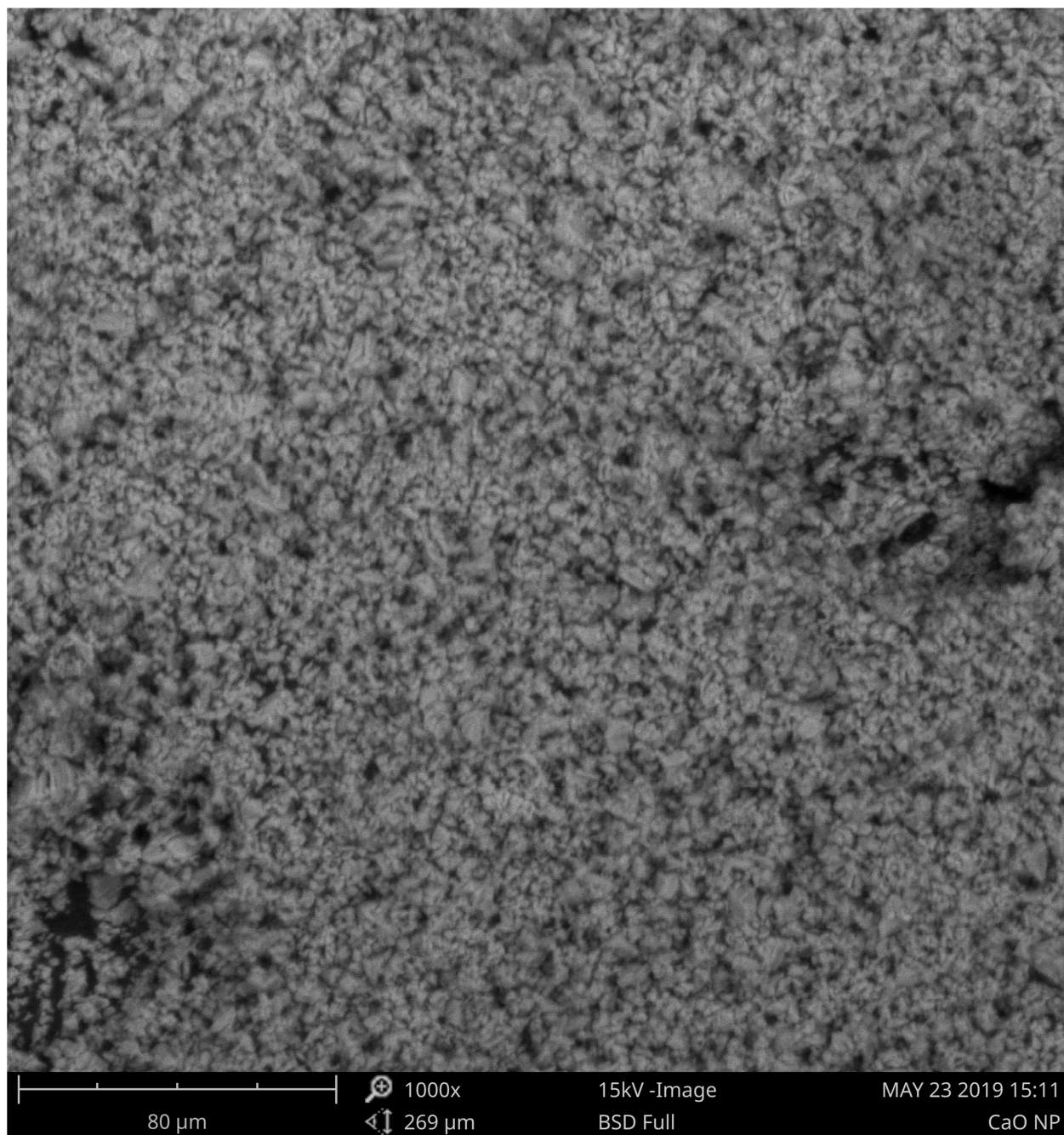


Figure 3. 80um 15kV-image of CaO nanoparticles.

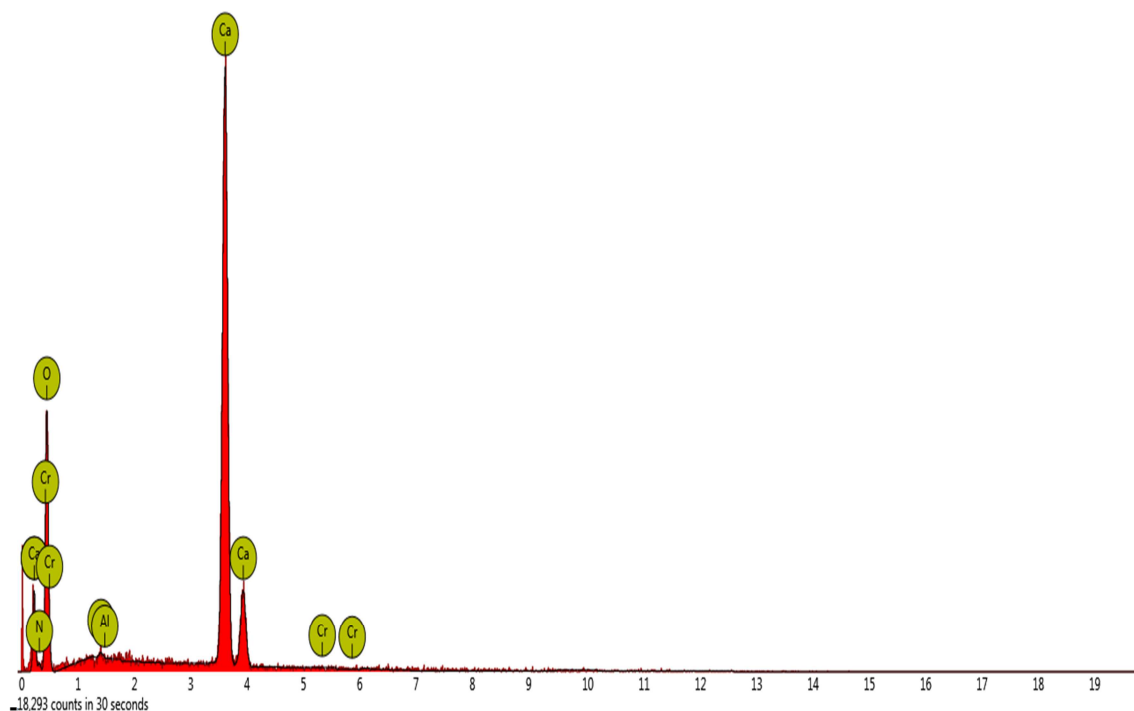


Figure 4. ED Spectral image of calcium oxide nanoparticles synthesized from chicken eggshell.

D. Thermo gravimetric Analysis (TG-FTIR) result

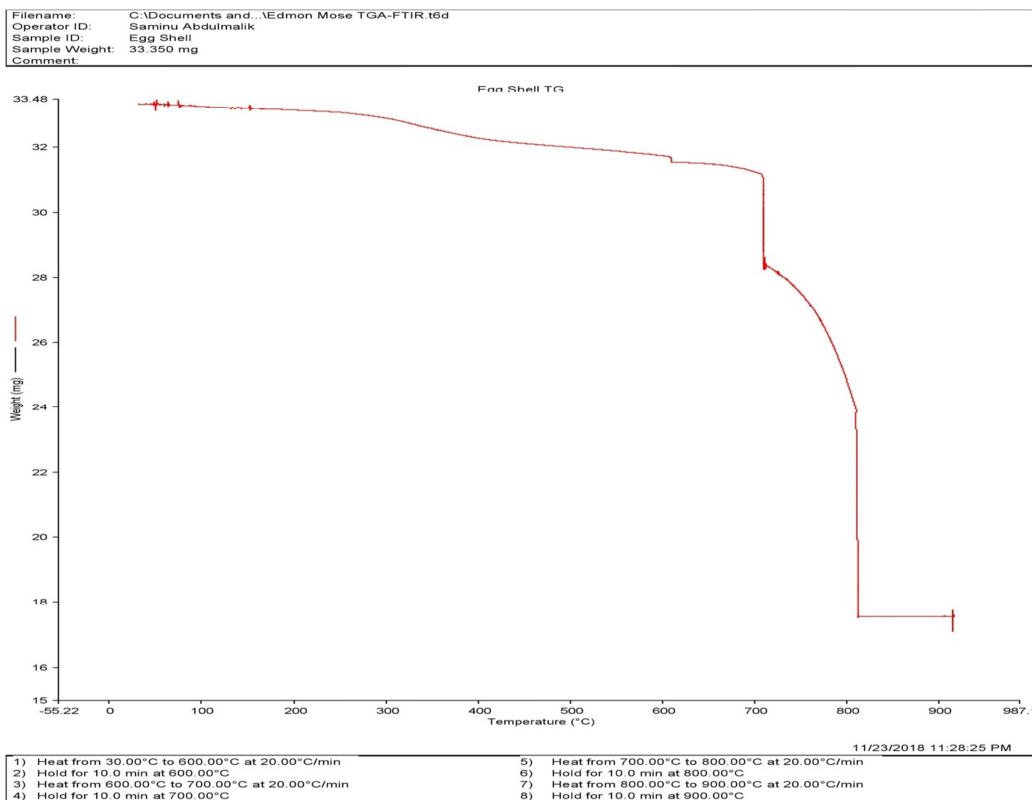


Figure 5. Thermal Analysis of CaO nanoparticles.

Figure 5: shows the thermal transitions during the reaction process were described by TG-FTIR. 33.48 mg of the sample was used. The figure indicates that the degradation in nanoparticles occurred in four phases, when the temperature is varied from 0° C to 900 °C. Initially, mass loss starts at about 250 °C to 32.00 mg due to the hydration of water contents. The second mass loss slightly occurred at 600 °C to 31,00mg attributing to the exhaustion of ethanol used in chemical reactions. The third mass loss occurred at 700 °C to 26.00 mg. The rapid mass change was observed in the fourth phase at 800 °C to 17.00 mg, and the

last mass loss is observed at 900 °C to 16.30 mg. This variation is due to the phase change from CaCO₃ and other elements in to CaO phase which is also confirmed by X-ray diffraction. The calcination continued to ensure complete conversion into CaO. The decomposition of the carbonate was accompanied by evolution of CO₂, according to the following endothermic reaction;



E. Fourier Transform Infrared Spectroscopy Analysis for the control (uncalcined chicken eggshell)

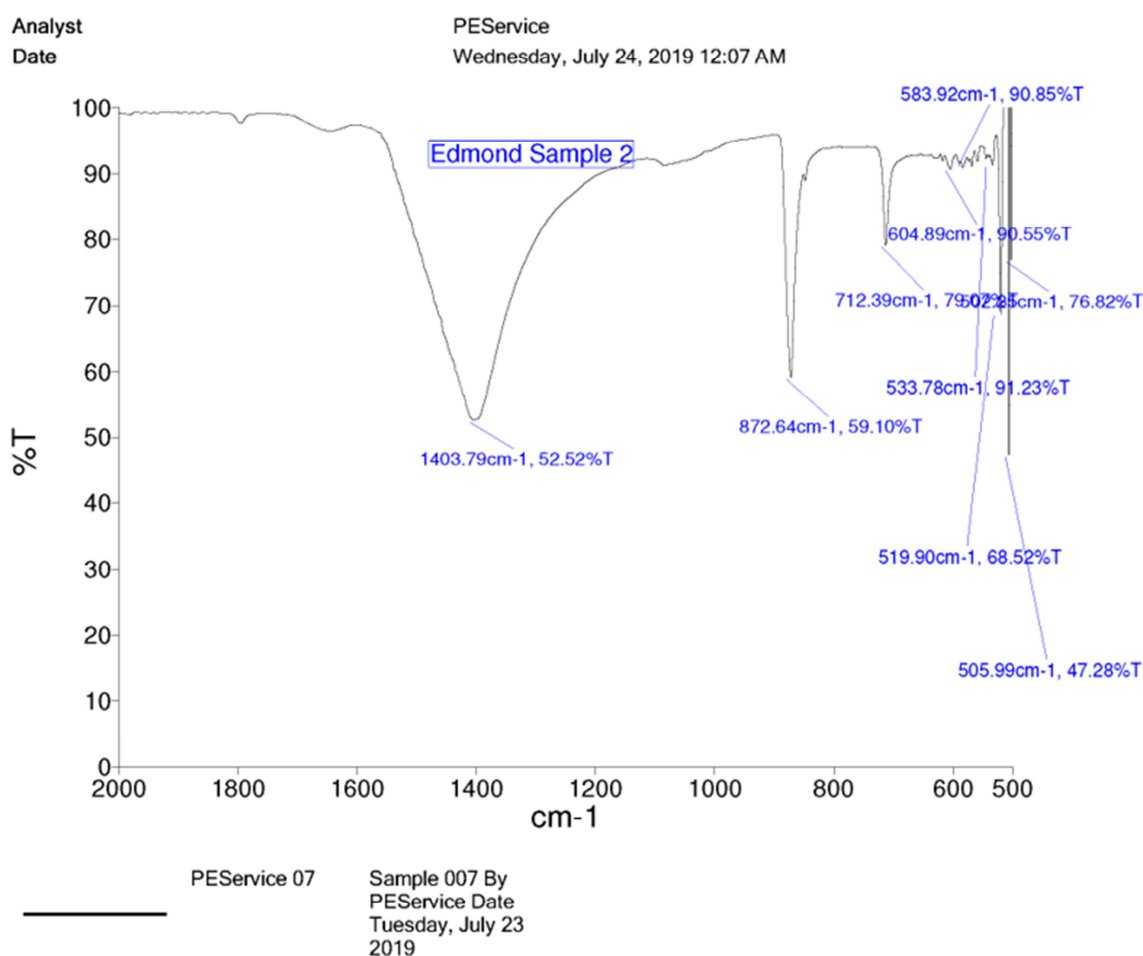


Figure 6. FTIT result for the uncalcined chicken eggshell (control).

The absorption between 870 cm⁻¹ – 675 cm⁻¹ is a strong band bending C – H of a phenyl ring constituent. At absorption of 873cm⁻¹, it shows a weak band of C – O bond related to carbonation of Calcium oxide nanoparticle. At absorption band of 553 cm⁻¹, it identifies the vibration of the

Ca – O bond. Generally, the sharp absorption around 720 cm⁻¹ to 924 cm⁻¹ indicates that the CaCO₃ as the basic component in eggshells are much available.

F. Fourier Transform Infrared spectroscopy for the CaO nanoparticle

The strong band at 3641.68 cm^{-1} corresponds to the free OH bonds stretching only in a dilute solvent from the remaining hydroxide. The bands at 1412.06 cm^{-1} corresponds to vibrational group for Amides, $\text{C}-\text{C}(=\text{O})$, this clearly shows C-N and skeletal stretching. Generally, the

absence of a sharp absorption around 724 cm^{-1} and 924 cm^{-1} indicates that the Calcium Carbonate (CaCO_3) as the basic component of the eggshell are no longer present as it is already converted to CaO. This is in line with the research reported by (Risfidian *et al.*, (2016).

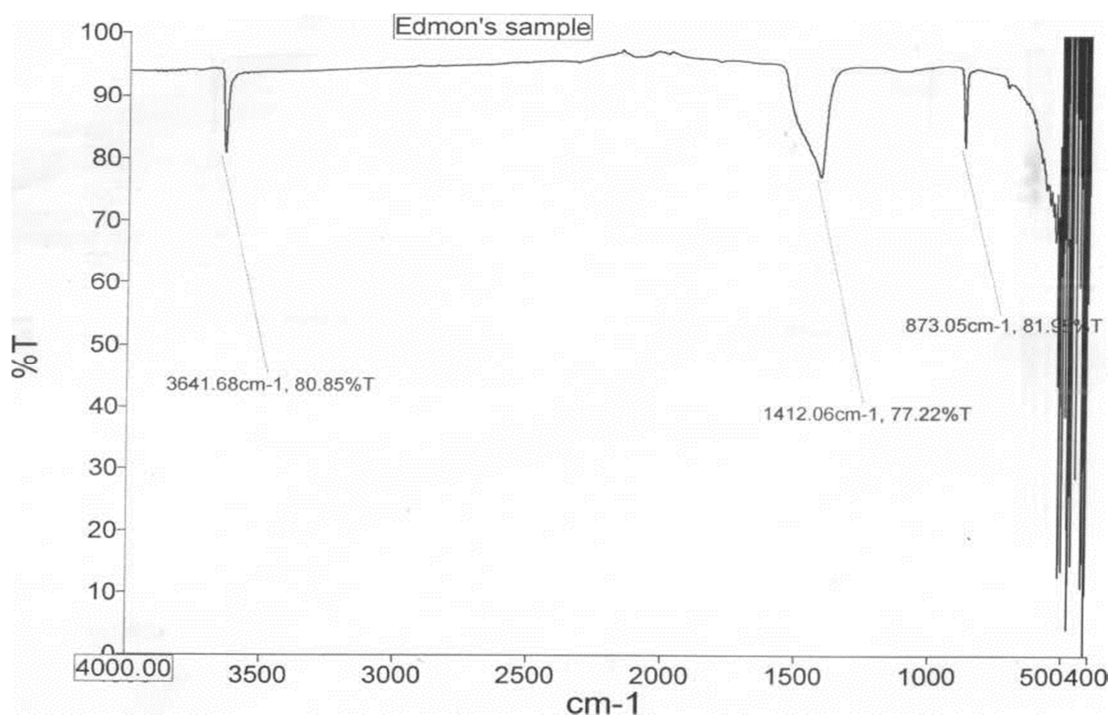


Figure 7. FTIR analysis of calcium oxide nanoparticle produced from chicken eggshell.

Table 3. Observed infrared band positions and their assignments of CaO.

Frequency	Vibrational group	Remark
3641.68	Primary aliphatic alcohol	Free OH stretching, only in dilute solution
1412.06	Amides, $\text{C}-\text{C}(=\text{O})-\text{NH}_2$	C-N and skeletal stretching

IV. CONCLUSION

In conclusion, CaO nanoparticle was synthesized from a chicken eggshell by the means of Chemical O-precipitation of the wet chemical synthesis method and this process basically be classified under the Bottom-Up process of production of nanopartiles. This shows the utilization and recycling of household wastes and the recycling process may also be performed on other household wastes. The XRF analysis of the particle shows that the chemical composition of the particle is 98.64%. This shows the perfection, precision and accuracy of the procedure utilized during the processes. The elemental composition shows that the larger composition of the substance is the Ca with 56.65% and 43.35% oxygen. SEM analysis shows that the particle size is nearly cubic in shape and the approximate size of the particle was calculated using Debye Scherrer equation and found to be 23.76nm. The Energy Dispersive spectroscopy of the substance shows the highest optical dispersion of Ca at 3.5keV while oxygen shows optical dispersion at 0.50KeV. Thermogravimetric analysis shows that the synthesized particle is thermally stable, 50% of the particle show perfect stability even at temperature of 950°C. FTIR analysis of the synthesized particle shows very limited signals on the absorption band and this clearly indicates the total conversion of the main components of eggshell (CaCO₃) into CaO nanoparticle.

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