EVALUATING THE PROPERTIES OF NANOPARTICLES OF CALCIUM CARBONATE OBTAINED FROM THE SHELLS OF AFRICAN GIANT LAND SNAILS (*ACHATINA ACHATINA*) VIA *IN SITU* DEPOSITION TECHNIQUE

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Nanoparticles of calcium carbonate were synthesized from the shells of African giant land snails through in situ deposition technique. The synthesized powder was characterized with x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric-differential thermal analyzer/differential scanning calorimeter (TGA-DTA/DSC thermal analyzer), transmission electron microscope (TEM), pH meter and density measurements. Both XRD and FTIR results showed that the synthesized nanoparticles are composed of the calcite and aragonite phases with more than 99 % purity. The crystallite size estimated from the XRD diffractogram at maximum intensity for the calcite phase was 22 nm while that of the aragonite phase was 35 nm. The average size of the particles estimated from TEM images was 50 nm while the density and pH were 2.81 g/cm^3 and 8.1 respectively. The TGA curve showed that the weight loss of the synthesized nanoparticles with temperature was a two-stage process with the first stage occurring between 281.39 ^{0}C and 313.31 ^{0}C, while the second stage started at 570 ^{o}C and completed at 850 ^{o}C. The DTA/DSC curve showed an exothermic peak between 281.39 ^{0}C and 313.31 ^{0}C. The properties of the synthesized powder show that the materials will be useful as filler in the composite industry as well as other areas.

Keywords: calcium carbonate, nanoparticles, properties, snail shells, characterization

1. Introduction

Calcium carbonate ($CaCO_3$) is a very important chemical for diverse industrial applications. Commercial $CaCO_3$ is used as a semi reinforcing filler in the rubber industry to reduce cost and improve processing characteristics [1-2]. It

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has also found applications in the paints, lubricants, ink, paper, plastics, adhesives, ceramic materials, toothpaste, food and paper industries [3]. Commercial $CaCO_3$ is in the form ground $CaCO_3$ (GCC) or precipitated $CaCO_3$ (PCC). PCC imparts higher mechanical properties in composites because of its smaller particle size. With advancement in technology, $CaCO_3$ as nanoparticles are being produced [2]. Nanoparticles of calcium carbonate have been synthesized by *in situ* deposition technique from a solution of calcium chloride [4-6]. Nanoparticles of calcium carbonate were synthesized from coockle shells also by *in situ* deposition technique [7]. Nanoparticles of $CaCO_3$ have been synthesized from the shells of fresh water channeled applesnail (*Pomacea canaliculata*) using similar technique [8]. The performance of nanoparticles of $CaCO_3$ as filler in composite materials has been compared with that of commercial calcium carbonate. Compared to commercial $CaCO_3$, nano $CaCO_3$ offered higher improvement in tensile strength, elongation at break, modulus at 300 % elongation, hardness, abrasion resistance, flame retardance and swelling resistance as filler in styrene butadiene rubber (SBR) [5]. Nanoparticles of $CaCO_3$ obtained by [8] dispersed well in poly(vinyl chloride) (PVC) and improved its tensile strength and impact energy at 5 and 10 pphr respectively; and imparted comparable mechanical properties in the composites obtained as compared with commercial nanoparticles of $CaCO_3$. Unfilled polypropylene exhibited elastic modulus of 200 MPa, when filled with 4 wt% nano $CaCO_3$, its modulus increased to 1000 MPa and further increased to 1400 MPa at 10 wt% filler loading [4] (Mishra, *et.al.*, 2004). Also, nano $CaCO_3$ showed superior improvement in mechanical properties than flyash in styrene butadiene rubber [5]. The use of nano particles of $CaCO_3$ as filler in natural rubber latex has been reported to reduce the vulcanization time with filler loading because of the high interaction of natural rubber and nano $CaCO_3$ [9]. Further investigation reveals that nano $CaCO_3$ as filler in natural rubber reduces swelling, increases elastic modulus and tensile strength as the filler loading increases up to 10 pphr [9]. Land snail shells have been reported to be rich source of calcium carbonate [10 -11]. In this work, we synthesized nanoparticles of calcium carbonate from the shells of African Giant Snails via *in situ* deposition technique and characterized the synthesized particles to ascertain their suitability for industrial applications.

2. Materials and Methods

2.1 Production of Nanoparticles of Calcium Carbonate from the Shells of Giant Land Snails

The method developed by [6] for the synthesis nano $CaCO_3$ by *in situ* deposition technique from calcium chloride solution was adopted. Snail shells were collected from Akure (latitude 7^0 $15^{'}$ 9.22" N; longitude 5^0 11' 35.23" E) area in Ondo State, Nigeria. The shells were washed thoroughly to remove all

impurities from the surface, dried under the sun for ten days and thereafter dried in oven at 120 ^oC for one hour to remove all moisture. The shells were crushed with a hammer; ball milled into fine particles and sieved with British standard sieves to collect the particles below 75 µm. 150 g of the fine particles was reacted with 150 g of concentrated hydrochloric acid to give calcium chloride solution as shown in equation (1).

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g) + CaCl_2\,(aq) \quad \text{----- (1)}$$

Polyethylene glycol (PEG) 6000 was purchased from Sigma Aldrich Germany. 200 g of the PEG was diluted with 100 ml of deionized water and mildly heated to 60 ^0C to promote mixing. The solution from the reaction of snail shell and HCl was digested with the solution of PEG for 24 hours. 100 g of potassium bicarbonate was dissolved in 100 ml of deionized water. The solution of the potassium bicarbonate was added slowly to the digested solution, thoroughly stirred and left overnight for the precipitation of nanoparticles of calcium carbonate to take place. The nanoparticles formed was filtered, washed with deionized water dried in oven at 120 ^oC for 36 six hours.

2.2 Characterization of the Produced Nanoparticles

PANalytical XRD machine, model X'Pert^3 Powder was used to analyze the phases and crystalline structure of the nano-$CaCO_3$ produced by varying the diffraction angle (2θ) from 5^0 to 80^0 using scanning speed of 2^o/min. The crystallite sizes in nanometer for the various phases present in the sample were calculated using Debye-Scherrer equation [8] [12] as shown in equation (2); where K is Scherrer constant taken to be 0.89, L is the crystallite size in nanometer, θ is the 2θ shown in the x-ray diffractogram which is the diffraction angle in degree, β(2θ) is the diffraction peak width in radian at half height and λ is the wavelength of the x-ray in nanometer calculated to be 0.1789 nm from Brags equation shown in equation (3), where b is the interplaner spacing in nanometer and θ is the angle of incidence of the x-ray . All the data required for the calculation of the crystallite sizes were obtained from the x-ray diffractogram obtained. Crystallite sizes were measured at the diffraction angle with maximum intensity [8].

$$L = \frac{K\lambda}{\beta \cos\theta} \quad \text{---------- (2)}$$

$$\lambda = b\sin\theta \quad \text{---------- (3)}$$

Fourier Transform Infrared Spectra were obtained with IRAffinity-1 Shimadzu FTIR Spectrometer in the wave region 4000 - 340 cm^{-1} at room temperature (18 ^oC) using KBr pellet method. The FTIR spectra were obtained at the resolution of 4 cm^{-1} and mirror speed of 2.8 mm/sec.

The thermal properties of the produced nano-$CaCO_3$ were studied with TGA-DTA/DSC SETARAM Instrumentation Thermal Analyzer. 48.7 g of the sample was placed in the chamber and heated under an air atmosphere from room temperature to 800 ^{0}C at a continuous heating rate of 5 °C/min and air flow rate of 50 ml/min. The temperatures at the onset of loss and peak loss were evaluated. The heat flow during the process was evaluated.

The sample was characterized with Tecnai G2 Spirit-FEI transmission electron microscope (TEM) to obtain the images at accelerated voltage of 120 kV. Twenty TEM images obtained were analyzed to calculate the average particles size. In the calculation of the average particles size, the length and width of each particle were measured with respect to the resolution of the micrograph and the average calculated.

The density of the prepared sample was obtained using Archimedes principle as explained by [13] and pH was read from a pH meter in a suspension of the particles in deionized water [14].

3. Results and Discussion

The XRD diffractogram is shown in Fig. 1. The result shows similar diffraction pattern of nanoparticles of calcium carbonate as earlier synthesized and reported [6] [15]. Both calcite ($Ca_{6.00}C_{6.00}O_{18.00}$) and aragonite ($Ca_{3.99}Sr_{0.01}C_{4.00}O_{12.00}$) phases were identified at various diffraction angles. No other impurities were identified. The crystallites of the calcite phase were reported to be averagely hexagonal in shape while those of the aragonites were orthorhombic similar to the nanoparticles of calcium carbonate synthesized from the shells of apples snails reported earlier [8]. The crystallite size of the calcite phase estimated at 100 % intensity and angle 2θ equal to 34.267 ^{0} was 22 nm while the crystallite size of the aragonite phase estimated at 100 % intensity and angle 2θ equal to 30.543 ^{0} was 35 nm.

The FTIR spectra of the nanoparticles synthesized in this work is shown in Fig. 2. The vibrations associated with CO_3^{2-} ion absorption band are located within the 400 -1800 cm^{-1} regions. The strong vibration peak at 1423.47 to 1404.09 cm^{-1} is due to the assigned stretching of vibration of C=O in the carboxylate of $CaCO_3$ as reported [8]. The absorption bands observed at the vibration peaks at 875.63 and 1423 cm^{-1} are characteristics of calcite and similar to the work reported [16]. The in-plane bending modes of aragonite phase are observed in absorption band of 696 to 711.13 cm^{-1} [8]. The absorption bands observed in the regions 2800 to 3000 represents the vibration modes C-H on stearic acid [17-18].

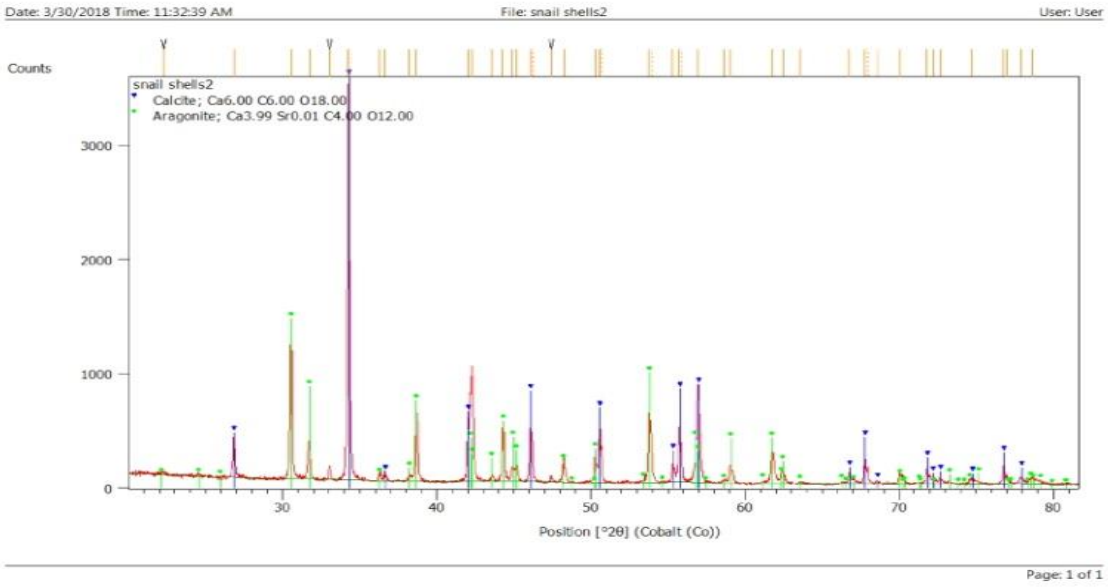


Fig. 1: XRD pattern of the synthesized nanoparticles from shells of African Giant Land snails.

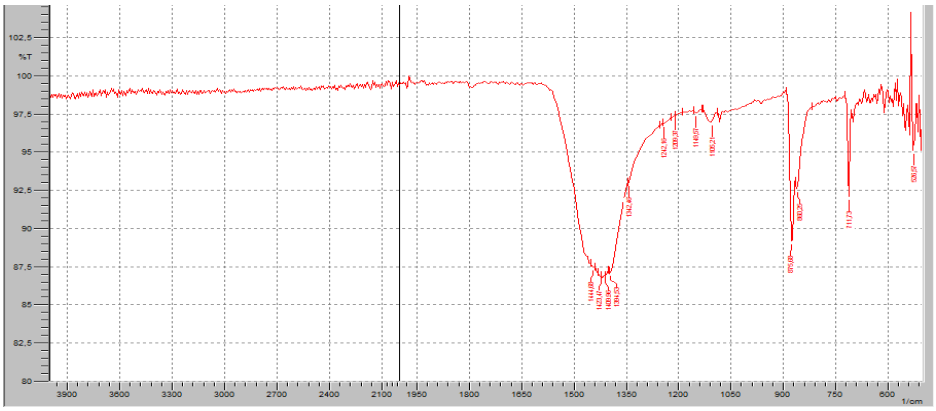


Fig. 2: The FTIR spectra the synthesized nanoparticles from shells of African Giant Land snails.

The TGA-DTA/DSC thermograms obtained are shown in Fig.s 3 and 4. In Fig. 3, the TGA curve shows the weight loss of the nanoparticles of $CaCO_3$ synthesized as a function of temperature and it is a two-stage process. The first stage of degradation started at 281.39 ^{0}C and completed at 313.31 ^{0}C with about 2.96 wt% loss (1.443 mg weight loss from 48.7 g). This first stage of decomposition corresponds to the degradation of stearic acid and organic materials [18]. The result is in agreement with earlier reports [8] [15]. The second stage of decomposition of the sample started at 570 ^{o}C and completed at 850 ^{o}C.

The second stage corresponds to the decomposition of $CaCO_3$ to form calcium oxide (CaO) and CO_2 [18]. In Fig. 3, DTA/DSC curve shows an exothermic peak between 281.39 ^{0}C and 313.31 ^{0}C due to the degradation of stearic acid [20]. From Fig. 4, it took about 5000 s for the thermal degradation process to be completed.

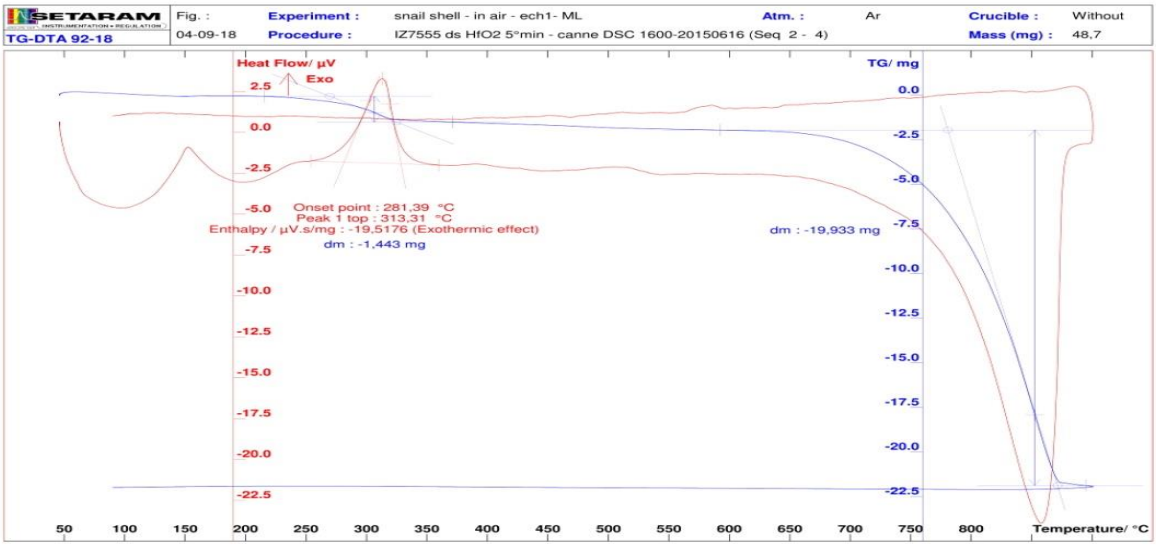


Fig. 3: TGA-DTA/DSC thermogram of the synthesized nanoparticles as a function of temperature

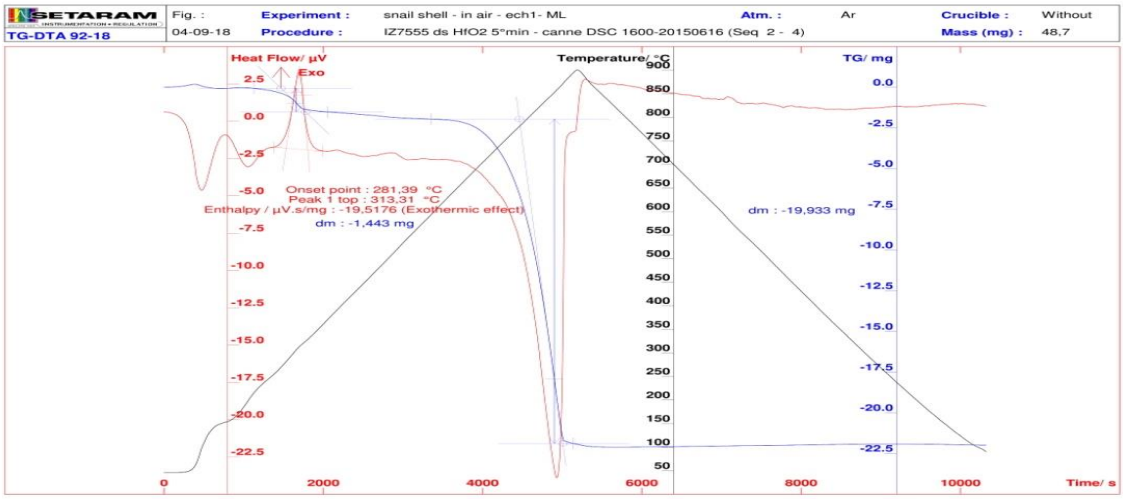
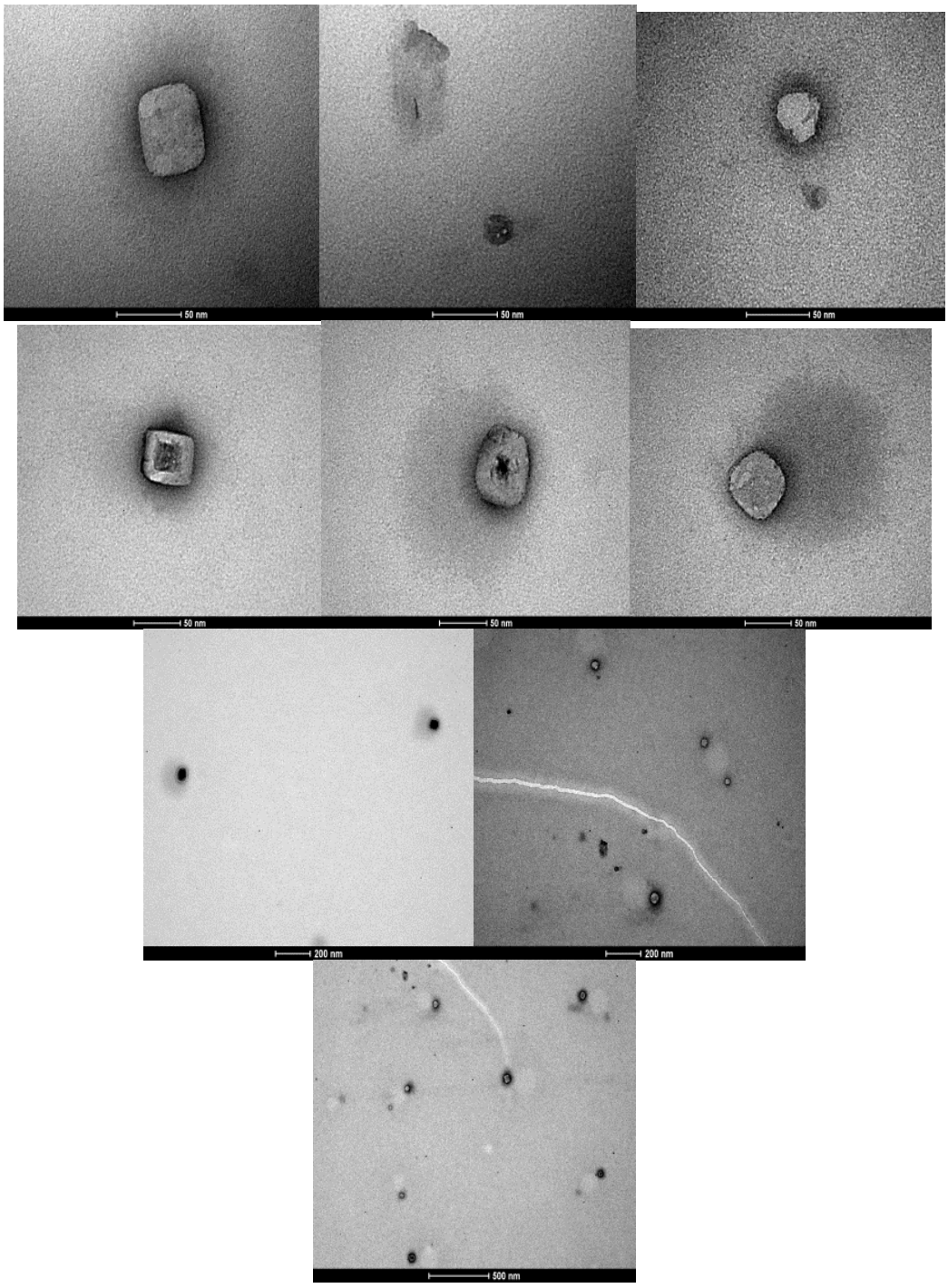


Fig. 4: TGA-DTA/DSC thermogram of the synthesized nanoparticles as a function of time

The orthorhombic shape of the aragonite phase and the hexagonal shape of the calcite phase in the synthesized nanoparticles are shown in the micrographs to support the XRD result as shown in Fig. 5.


50 nm
50 nm
50 nm
50 nm
50 nm
50 nm
200 nm
200 nm
500 nm

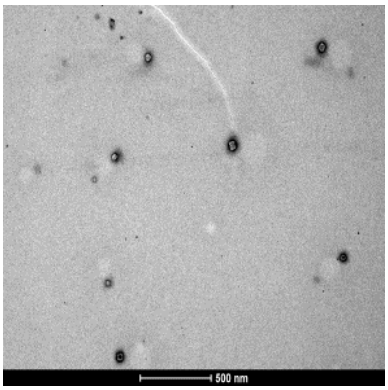


Fig. 5: Ten TEM micrographs of the synthesized nanoparticles at various resolutions.

The average particles size calculated from the TEM images is 50 nm. Spherical nanoparticles of $CaCO_3$ were shown in the micrograph synthesized by solid state treatment earlier reported [15].

The results of the crystal structure analysis generated with software attached to the XRD machine reported the density of the aragonite phase as 2.93 g/cm^3 and volume of cell as 226.92 x 10^6 pm^3; while the density of the calcite phase was 2.71 g/cm^3 and volume of cell as 368.08 x 10^6 pm^3. The density of the synthesized nanoparticles experimentally determined with Archimedes principle was 2.81 g/cm^3. The density value agrees with literature [21].

The pH obtained was 8.1. The value of pH also corresponds to literature [22].

4. Conclusions

Nanopaticles of $CaCO_3$ has been synthesized from the shells of African giant land snails vie *insitu* deposition technique. The process is simple. The results from the characterizations that were done show the high purity of the synthesized nanoparticles. We envisage the industrial application of this material especially in the composite industry. This research contributes in the areas of conversion of agricultural wastes to wealth.

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