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Synthesis and Characterization of Cassava Bark Nanoparticles

F.O. Kolawole[a,b,*], S.K. Kolawole[c], J.O. Agunsoye [b], S.A. Bello[b,d], J.A. Adebisi[b,e], W.O. Soboyejo[f], S.B. Hassan[b]

[a]*Department of Materials and Metallurgical Engineering, Federal University, Oye-Ekiti, Nigeria*

[b]*Department of Metallurgical and Materials Engineering, University of Lagos, Lagos, Nigeria*

[c]*National Agency for Science and Engineering Infrastructure, Abuja, Nigeria*

[d]*Department of Materials Science and Engineering, Kwara State University, Malete, Nigeria*

[e]*Department of Metallurgical and Materials Engineering, University of Ilorin, Ilorin Nigeria*

[f]*Department of Mechanical and Aerospace Engineering, Princeton University, New Jersey, U.S.*

Corresponding Author: funsho.kolawole@fuoye.edu.ng or fkopresido@yahoo.com

Abstract

Synthesis and characterization of cassava bark nanoparticles (CBNPs) was carried out using ball milling at 36, 48, 60 and 72 hours. The morphology study was done using SEM and the Gwyddion software was used to determine the particle sizes from the SEM images. The particle distribution for the un-milled cassava bark (CB) was between 1.25 ± 0.06 to 19.92 ± 1.00 µm, while after milling for 36, 48, 60 and 72 hours the average particle size were 4.07 ± 0.20, 4.00 ± 0.20 µm, 80.90 ± 4.05, 74.50 ± 3.73 nm respectively. 13.68 ± 0.68 nm was obtained by XRD using Scherrer equation after milling for 72 hours and the XRD results revealed the presence of compounds such as SiO_2, $CaCO_3$ and $KAlSi_3O_8$. TEM was used to determine nanoparticle size distribution after milling for 72 hours and the particle size ranged from 9.73 ± 0.49 to 114.60 ± 5.73 nm for cassava bark nanoparticles (CBNPs), EDX results showed trace element of Si, Ca, K, Fe, Al, O in the CB milled for 72hours.

INTRODUCTION

Agro-wastes which are dumped all over the environment and serves as nuisance are beginning to gain attention in different areas of application including composite, bio-gas, animal feed, bio-fertilizer [1-5]. The use of agro-waste for different applications helps to add value to waste materials and replace other items where cost and availability is considered [4-5]. It also provides cleanliness to our environment.

The botanical name for Cassava is *Manihot esculenta*, it is a woody shrub of the spurge family, Euphorbiaceae from South America. It is commonly cultivated annually in the tropical and sub-tropical regions for its edible starchy tuberous root (carbohydrate source) [6]. World production of cassava root was estimated to be 245 million tonnes in 2012, while production in Africa was about 137 million tonnes, being the largest contributor to the world production; 75 million tonnes was produced from Asia and 33 million tonnes from Latin America and the Caribbean (mainly from Jamaica). Nigeria is the world's largest producer of cassava, producing about 54 million tonnes annually [7].

Cassava bark (CB) consist of two layers namely; the outer skin and inner skin [8], both layers combine together serves as agro-waste and since annual production of cassava is high, it implies that the amount of agro-waste that can be generated from cassava bark is significant which can be converted to useful products, it has also been reported that the bark alone consist of 5 – 10% of the cassava root [8-10]. CB is used for animal feed [8], biogas [10], and other application.

Nanoparticles may be created using several methods and can be classified into two, namely: Top-Down; attrition, milling and Bottom-Up; pyrolysis, inert gas condensation, solvothermal reaction, sol-gel fabrication and structured media. [11-12]. When considering the type of method to be used, the following features need to be considered in order to achieve the desired nanoparticles; control of particle size, size distribution, shape, crystal structure and composition distribution; large surface area; improvement of the purity of nanoparticles (lower impurities); control of aggregation; stabilization of physical properties, structures and reactants; higher reproducibility; higher mass production, scale-up and lower costs [11].

Synthesis of CB nanoparticle could be used for various applications and also a waste management strategy for the environment. This research work is focused on the synthesis and characterization of cassava bark nanoparticles (CBNPs). Top-down approach (mechanical milling) was used to synthesize and characterize CBNPs.

MATERIALS, EQUIPMENT AND METHODOLOGY

Materials and equipment

CB which was used for this work was obtained from farmers in Ayedun-Ekiti, Nigeria. The equipment used include commercial grinding machine in Ilorin, Kwara State, Nigeria, ball milling machine in FIIRO, Lagos, Nigeria, sieve shaking machine and digital weighing scale in FUTA, Akure, Nigeria. Other equipment used was scanning electron microscope (SEM) attached with EDX and Gwyddion software, X-ray diffraction spectroscopy (XRD) and transmission electron microscope (TEM) in University of Pretoria, South Africa.

METHODOLOGY

Synthesis of cassava bark nanoparticles

Cassava bark was soaked in water for 24 hours, in order to reduce the level of cyanide acid. After which the cassava bark was sun dried for 14 days. The dried cassava bark was grounded using a commercial grinding machine and were sieved using a sieve shaking machine for 1 hour. The sieve sizes range from 53 to 150 µm. CB powders used for the synthesis of nanoparticles was obtained from below 150 µm**.**

200 g of CB powders were placed in an E3 sized vial containing 5 – 600 mm sized ceramic balls having a total mass of 2 kg. The CB powders was milled for 36, 48, 60 and 72 hours, according to similar methods used by Bello et al, 2015 [13], at 6 hours per day. The milling was carried out at a speed of 195 rpm, under dry grinding conditions at time intervals of 36, 48, 60 and 72 hours. Samples were taken from each of the powders at the different milling times intervals for analysis.

Characterization of CBNPs

Scanning electron microscope (SEM) with EDX/Gwyddion software was used to study the morphology and chemical elements of all the samples at the different intervals. X-ray diffraction spectroscopy (XRD) was used to determine the element present and analysis the particle size of each of the CBNPs. Transmission electron microscope (TEM) was used for particle size analysis.

SEM/EDX

The SEM and EDX were obtained using a Zeiss Ultra Plus 55 field emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 1.0 kV. EDX was performed with the same system operated at 20 kV. SEM images were taken for un-milled and milled samples (36, 48, 60 and 72 hours) for the cassava bark. Gwyddion software was used to determine the minimum, maximum, average and median particle size of the un-milled and milled powder. Furthermore, EDX was used to determine trace elements in CB after 72 hours of milling.

XRD

Powder X-ray diffraction (XRD) was recorded in the 2θ range between 20.0–80.0 using an XPERT-PRO diffractometer (PANalytical BV, the Netherlands) with theta/2theta geometry and a counting time of 15.240 seconds per step. Qualitative phase analysis of samples was conducted with the X'pert Highscore search match software at room temperature using Co K1α (ƛ=0.178897 nm). XRD was used to analyze samples of cassava bark milled for 72 hours, the particle size was analyzed using Scherrer equation as reported by Monshi, et al, 2012 [14].

$$L = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Where L is particle size, λ is the X-ray wavelength in nanometer (nm), β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken

as 0.9. The value of β in 2θ axis of diffraction profile must be in radians [14]. The wavelength used for the samples was $\lambda Cok\alpha_1 = 0.179$ nm.

TEM

TEM was carried out using JEOL Transmission Electron Microscope (Model: JEM-2100F Multipurpose Field Emission TEM) to analyze the samples from the cassava bark milled for 72 hours to determine the particle size.

RESULTS AND DISCUSSIONS

SEM micrographs

The surface morphology of the un-milled CB is shown in **Fig. 1a**, which reveals that the microstructures of the CB has a wide range of different particle size and shape with some of them being spherical. The minimum, maximum, average and median particle sizes of the SEM images for the un-milled sample were obtained using Gwyddion software. The minimum, maximum, average and median particle sizes for the CB were 1.25 $\pm$ 0.06, 19.92 $\pm$ 1.00, 10.19 $\pm$ 0.51 and 10.2 $\pm$ 0.51 µm respectively. **Fig. 1b-e** shows micrographs of CB milled at different time intervals (36, 48, 60 and 72 hours). **Fig. 1b** reveals microstructure of CB milled for 36 hours, having a closer range of different particle size and shape compared to **Fig. 1a** this was as a result of milling for 36 hours; the average particle size obtained was 4.07 $\pm$ 0.20 µm. From **Fig. 1c-e** it can be observed that as the milling time increased from 48 – 72 hours, there is a decrease in particles size and particles became uniform and evenly distributed in size and spherical in shape. **Fig. 1c-e** reveals microstructure of CB milled for 48, 60 and 72 hours, the average particle size obtained was 4.00 $\pm$ 0.20 µm, 80.90 $\pm$ 4.05 and 74.50 $\pm$ 3.73 nm respectively. From the results nanoparticles were observed after milling for 60 hours. **Fig. 1f** shows the EDX result of CB after milling for 72 hours which showed trace elements such as Si, Ca, K, Fe, Al and O which could serve as alloying elements, strengthen mechanism in composites, etc.

From **Fig. 2**, the particle size distribution indicates that nanoparticles are obtained after milling for 60 hours. From the bar chart it can be seen that as milling time increase there was a decrease in particle size, the minimum particle size that was obtained for un-milled, 36, 48, 60 and 72 hours of milling ranges from 1.25 $\pm$ 0.06, 0.77 $\pm$ 0.04, 0.60 $\pm$ 0.03 µm, 43.90 $\pm$ 2.20 and 27.50 $\pm$ 1.38nm respectively.

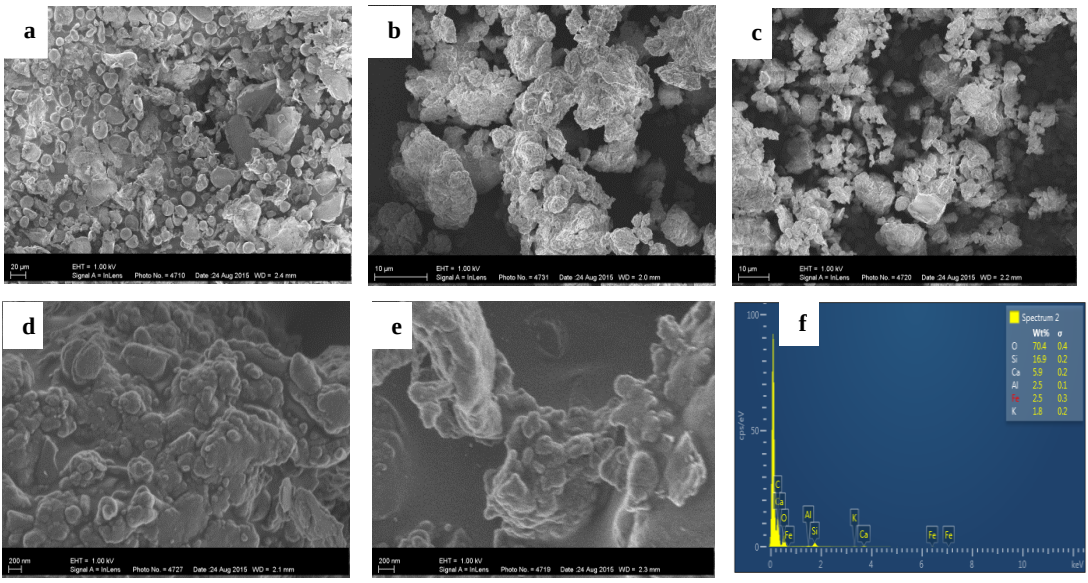

Fig. 1: SEM of cassava bark (a) un-milled (b) milled for 36 hours (c) milled for 48 hours (d) milled for 60 hours (e) milled for 72 hours (f) EDX of CB milled for 72 hours

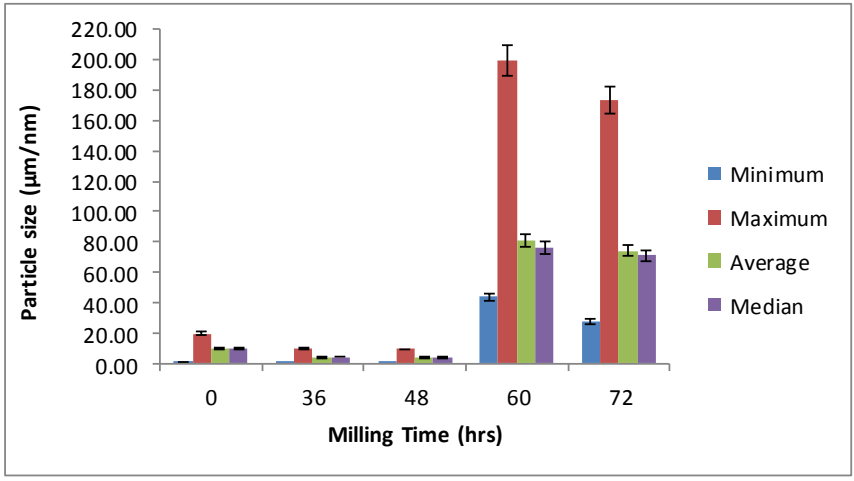

Fig. 2: Bar chart showing the minimum, maximum, average and median particle size of CBNPs

XRD analysis

From the XRD result shown in **Fig. 3**, the major peaks occurred at diffraction angles (2Θ) of 30.5, 31 and 34.2°. Peak representing each phase is indicated by vertical line painted in different colours for the purpose of phase identification. The particle size was estimated using Scherrer equation as reported by Monshi et al. 2012 [13]. The particle size obtained after milling for 72 hours was 13.68 ± 0.68 nm for CB. The XRD results using the Scherrer equation indicates that CBNPs can be obtained after milling for 72 hours. Compounds such as SiO_2, $CaCO_3$ and Al_2O_3, Ca_3SiO_5 and $KAlSi_3O_8$ were revealed from the XRD result.

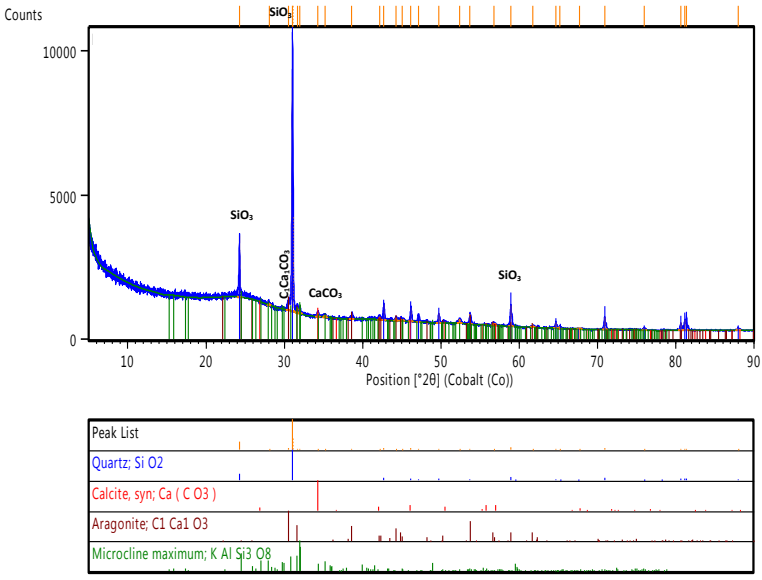

Fig. 3: XRD of CBNPs obtained after milling for 72 hours

TEM micrographs

The TEM image which was taken for CB milled at 72 hours at a resolution of 100nm shown in **Fig. 4**, revealed an accurate particle size compared to that obtained from SEM. The particle size was spherical in shape and was determined by placing a red perpendicular line at the centre of the particle from top to bottom as shown in the TEM images. The average particle size that was obtained after 72 hours of milling was 15.23±0.76 nm for CBNPs. The particle size distribution for the TEM image for the CBNPs is represented in **Fig. 5**. The particle size distribution shows that majority of the particle size were within the range of 20 nm. The particle size that was obtained from the XRD and TEM 13.68 ± 0.68 nm and 15.23±0.76 nm respectively, showed a close correlation in size, which in agreement with what has been reported by Ghandoor et al. 2012 [15], while that obtained from the SEM/Gwyddion software was 27.50 ± 1.38 nm.

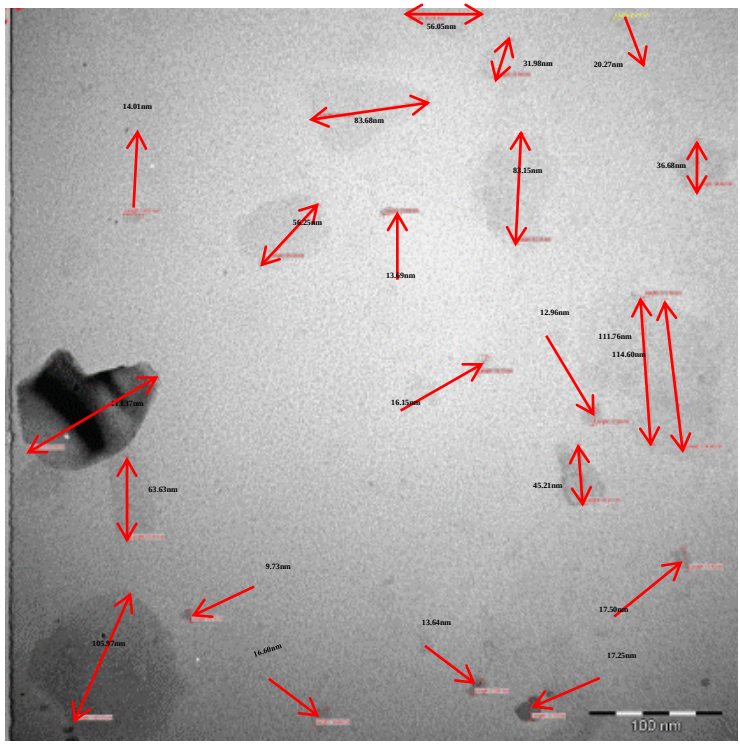

Fig. 4: TEM image of CBNPs milled for 72 hours

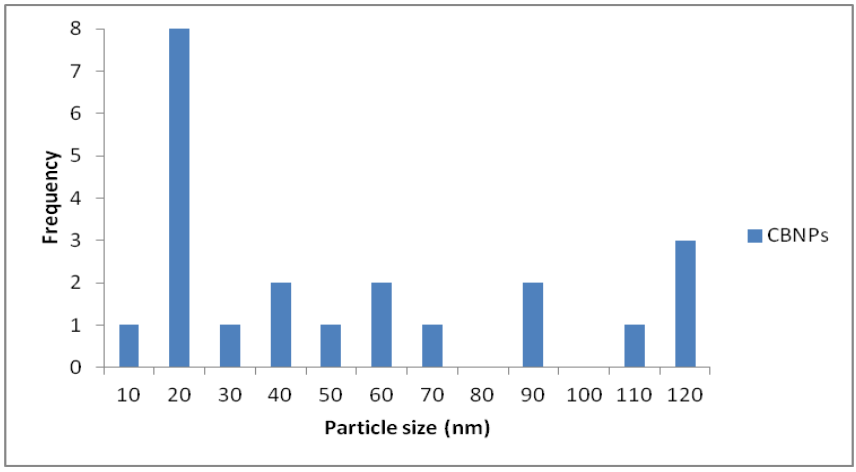

Fig. 5: Particle size distribution for CBNPs after milling for 72 hours obtained from TEM

CONCLUSION

This research work shows that CBNPs can be obtained after milling for 60 hours. The average particle size were estimated by SEM/Gwyddion software, XRD and TEM. The particle distribution for the un-milled cassava bark (CB) was between 1.25 $\pm$ 0.06 to 19.92 $\pm$ 1.00 µm, while after milling for 36, 48, 60 and 72 hours the average particle size were 4.07 $\pm$ 0.20, 4.00 $\pm$ 0.20 µm, 80.90 $\pm$ 4.05, 74.50 $\pm$ 3.73 nm respectively. 13.68 $\pm$ 0.68 nm was obtained by XRD using Scherrer equation after milling for 72 hours. Trace elements such as Si, Ca, K, Fe, Al and O was revealed through the EDX result, XRD result it revealed compounds such as SiO_2, $CaCO_3$ and Al_2O_3, Ca_3SiO_5 and $KAlSi_3O_8$ that can help in improving the mechanical properties of alloys or composite and other applications. This work shows that the CBNPs can be produced and used for some applications, thereby adding value to the CB that is usually dumped and also reduce pollution to the environment.

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