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Particle Size Analysis and Characterization of Cassava (*Manihot esculenta crantz*) Stem Nanoparticles (CSNPs) via a Top-down Approach

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Abstract

Characterization of synthesized cassava stem nanoparticles (CSNPs) was carried out using SEM/EDX and Gwyddion software, XRD and TEM for cassava stem (CS) ball milled at 36, 48, 60 and 72 h. The morphology study was done using SEM and the Gwyddion software was used to determine the particle size from the SEM images. The particle size range for the un-milled cassava stem (CS) was between 1.02± 0.05 to 19.99± 1.00 µm. After milling for 36, 48, 60 and 72 h the average particle size were 0.93±0.05 µm, 128.20± 6.41, 111.20± 5.56, 101.20 ± 5.06 nm respectively. The particle size of 11.83±0.59 nm was obtained by XRD using Scherrer equation after milling for 72 h and the XRD results revealed the presence of compounds such as SiO_2, $CaCO_3$, Ca_3SiO_5 and Al_2O_3. Furthermore, TEM was used to determine nanoparticles after milling for 72 h and the particle size ranged from 8.35 ± 0.42 to 51.74 ± 2.59 nm for cassava stem nanoparticles (CSNPs) and EDX result showed trace element of O,Si, Ca, Al, K, Ti, Fe andP in the CS milled for 72 h.

Keywords: Cassava stem; Nanoparticles; Synthesis
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1.0 Introduction

Nanoparticles of various types has been synthesized; gold (Adetunji, et al, 2015), silver (Lue, 2007), magnetite (Ghandoor, et al, 2012; Lue, 2007), zinc oxide (Vanaja and Rao, 2015), silicon oxide (Lue, 2007), and others, which can be synthesized using various methods such as the breakdown (top-down) method by which an external force is applied to a solid that leads to its break-up into smaller particles; sub-divided into grinding system (dry and wet), mechanochemical method (mills and ultrasonic wave) and mechanical alloying method. The second is the build-up (bottom-up) method that produces nanoparticles starting from atoms of gas or liquids based on atomic transformations or molecular condensations; chemical vapor deposition (CVD: flame, plasma, laser, electric furnace), physical vapor deposition (PVD), thermal decomposition method, plasma, electron beam, laser, chemical reduction method, indirect reduction method, solvothermal synthesis and sol-gel/gel-sol (Holister, et al, 2003; Horikoshi and Serpone, 2013).

Agro-wastes are gaining increasing attention these days, due to the fact that they can be processed into other useful products for various applications such as bio-gas, animal feed, bio-fertilizer, pulp and paper, leather, alcohol production and other engineering applications (Abba, et al, 2013; Akaranta, 2007; Ezejiofor, et al, 2014; Ibrahim and Mumtaz, 2014; Prasertsan, et al, 2007; Ibrahim and Mumtaz, 2014; UNEP, 2009). Globally, 140 billion metric tonnes of biomass is generated every year from agriculture, which is dumped all over the environments in the world and they serve as a nuisance to the environment until being put into proper use (Abba, et al, 2013; Prasertsan, et al, 2007). Cassava stems are the largest waste generated from cassava plantation after harvest, up to 400 bundles can be obtained per hectare (IITA, 2015). From the estimated amount of cassava, stem waste generated it shows that enough can be obtained for processing into a useful application. Cassava stems can be fed to pigs, poultry, dairy cattle and biochar production (Adetunji, et al, 2015; Noor, et al, 2012).

This research work focuses on synthesizing cassava stem nanoparticles (CSNPs) from cassava stem (CS) using a top-down approach (ball milling). The CS was milled at different milling times (36, 48, 60 and 72 h) and characterized.

2.0 Materials and Methods

Cassava stem was soaked in water for 24 h, in order to reduce the level of hydrocyanide, (HCN), content and sun dried for 14 days. The dried cassava stem was ground using a commercial grinding machine and was sieved using a sieve shaking machine for 1hour. CS powder used for the synthesis of nanoparticles was obtained from range of 150 to 53µm**.** 200 g of CS powders were placed in an E3 sized vial containing 5 – 60mm sized ceramic balls having a total mass of 2kg. The CS powder was milled for 36, 48, 60 and 72 h, at 6 h per day and at a speed of 195 rpm, under dry grinding condition. Samples were taken from each of the powders at the different milling time intervals for analysis.

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 2.0 kV. EDX was performed with the same system operated at 20 kV. SEM images were taken for unmilled and milled samples (36, 48, 60 and 72 h) for the cassava stem. Gwyddion software was used to determine the minimum, maximum, average and median particle size of the SEM images for both unmilled and milled samples. Furthermore, EDX was used to determine trace elements in CS after 72 h of milling. 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 sec per step. Qualitative phase analysis of samples was conducted with the X'pertHighscore search-match software at room temperature using Co $k_{1\alpha}$ (λ=0.178897 nm). XRD was used to analyze samples of cassava stem milled for 72 hours, the particle size was analyze using Scherrer equation as reported by Monshi, et al, 2012.

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

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 (Monshi, et al, 2012). The wavelength used for the samples was $\lambda Cok\alpha_1$ = 0.178897 nm. TEM was carried out using JEOL Transmission Electron Microscope (Model: JEM-2100F Multipurpose Field Emission Tem) to analyze samples of cassava stem milled for 72 h, in order to determine the particle size.

3.0 Results and Discussion

The CS morphology of the un-milled and that which was milled for 36 h (Fig. 1a-b)reveals microstructures of CS having random particle size and shape, with few of them being spherical.The microstructure also reveals agglomeration of particles and discrete particles. At this stage of milling, the CS powder particles were flattened by the compressive forces due to the collision of the ceramic balls.The particle sizes and morphologies of CSNPs were different as the milling duration increases (Fig. 1c-e) from 48 to 72 h. The CSNPs reveals agglomeration of fine particles and few discrete fine particles as the milling duration increases.

The increase in agglomeration of fine particles is due to continuous fracturing and cold welding of CS powder particles. The cold welding is attributed to the heat generated during the impact of the ceramic balls on the CS powder and the wall of the vial. As the milling duration increases there is an increase in agglomeration of fine particles and reduction in discrete fine particles (Fig. 1c-e). The fracturing of particles is a function of the impacts received by the particles from the milling balls with high kinetic energy. During the impacts, kinetic energy transferred by the milling balls to the particles is transformed into heat energy which raises the temperatures of the CSNPs. The heating effect leads to evaporation of the moisture contents of the CS particles. This makes the particles brittle and enhances their fracturing tendency, however resulting to particle softening which leads to particle agglomeration.The EDX spectrograph of the CSNPs obtained at 72 h of milling (Fig. 1f) indicates the presence of O, Si, Ca, Al, K, Ti, Fe and P (Table 1).

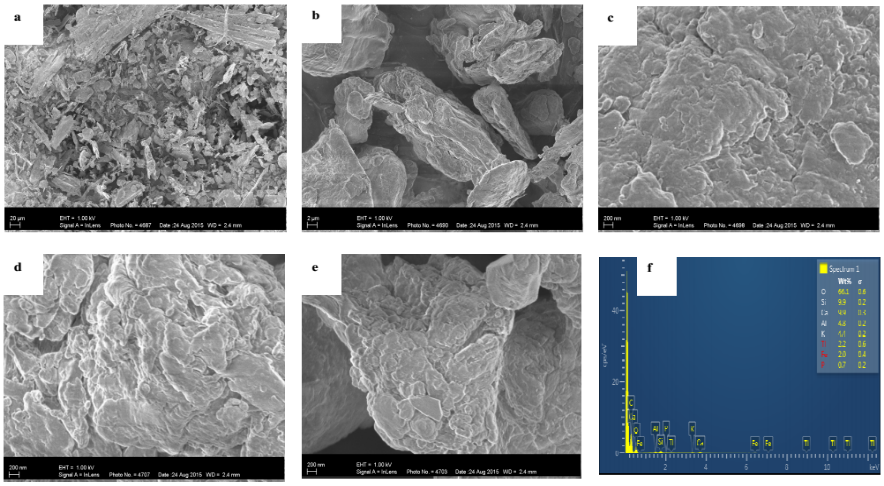

Figure 1: *Scanning Electron Microgram (SEM) of cassava stem (a) un-milled (b) milled for 36 h (c) milled for 48 h (d) milled for 60 h (e) milled for 72 h (f) Energy Dispersive Xray (EDX) of CS milled for 72 h*

Fig. 2 shows the particle size distribution and the particle size obtained were analyzed using SEM supported with Gwyddion software. The minimum, maximum, average and median particle sizes for the un-milled CS were 1.02 ± 0.05, 19.99 ± 1.00, 10.56 ± 0.53 and 10.82 ± 0.54 µm respectively. The average particle size obtained were 0.93 ± 0.05 µm, 128.20 ± 6.41, 111.20 ± 5.56, 101.20 ± 5.06 nm for CS milled for 36, 48, 60 and 72 h, respectively. The results also revealed nanoparticles were obtained after milling for 48, 60 and 72 hours. From the bar chart, it can be observed that as milling time increases, there was a decrease in particle size, the minimum particle size that was obtained for the CS milled for 48, 60 and 72 h respectively were 43.10 ± 2.16, 41.60 ± 2.08 and 25.10 ± 1.26 nm respectively (Fig. 2).

Table 1: Energy Dispersive X-ray Chemical Analysis of CSNPs milled for 72 h

Elements	% Composition
O	66.0
Si	9.9
Ca	9.9
Al	4.8
K	4.4
Ti	2.2
Fe	2.0
P	0.7

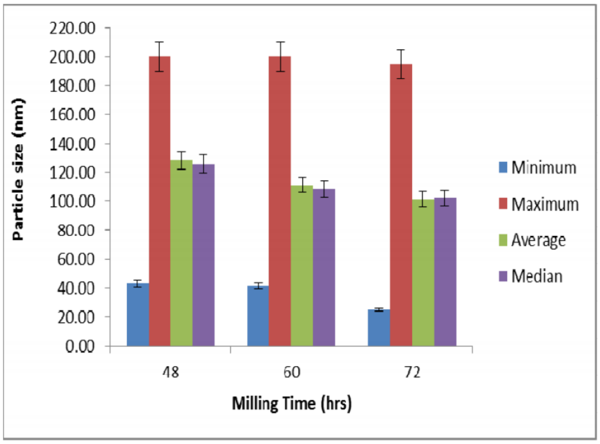

Figure 2: *Bar chart showing the minimum, maximum, average and median particle size of CSNPs*

The TEM image which was taken for CS milled at 72 h (Fig. 3B) at a resolution of 100nm, reveals a more precise particle size compared to that obtained from SEM (Fig. 1a-e). The particle 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 h of milling was 8.65±0.43 nm for CSNPs. CSNPs particle size distribution for the TEM image (Fig. 3C). The particle size distribution shows that majority of the CSNPs that appeared on the micrograph were within the range of 10 to 20 nm.

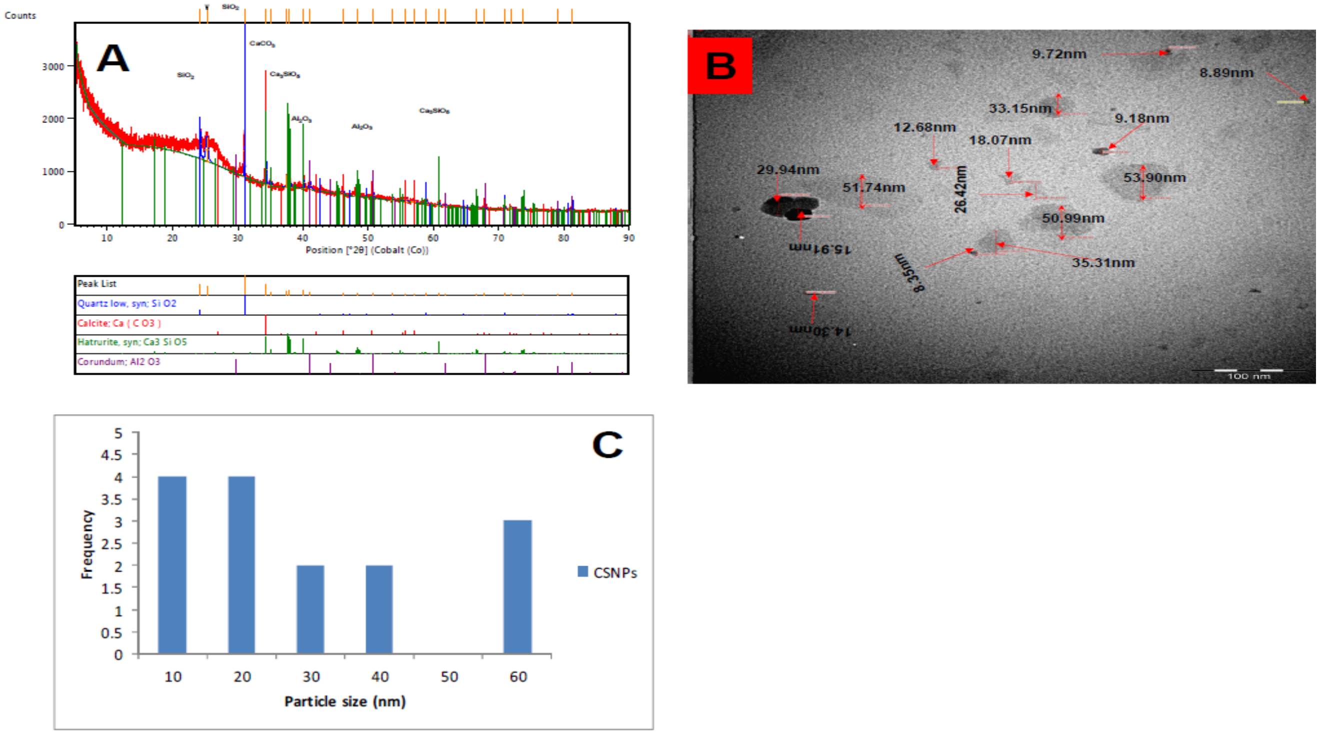

Figure 3: (A) Xray-Diffraction of CSNPs obtained after milling for 72 h (B) TEM image of CSNPs milled for 72 h (C) Particle size distribution for CSNPs after milling for 72 h obtained from TEM

The XRD result (Fig. 3A) indicates that the major peaks occurred at diffraction angles (2Θ) of 31, 34.2, 38 and 41^o, corresponding to SiO_2, $CaCO_3$, Ca_3SiO_5 and Al_2O_3 compounds respectively. Peak representing each phase are indicated by the vertical line in different colours for the purpose of phase identification. The most intensified peak which occurred at 31^o was used to estimate the particle size using Scherrer equation (see equation 1). The particle size of CSNPs obtained after milling for 72 h was 11.83 $\underline{+}$0.59 nm.

4.0 Conclusion

CSNPs were obtained after ball milling for 48 hours, the average particle size was estimated by SEM/Gwyddion software, XRD and TEM. There was a significant decrease in particle size as the milling time increased from 36 to 72 hours. The EDX result revealed trace elements such as O, Si, Ca, Al, K, Ti, Fe and P. XRD result revealed compounds such as SiO_2, $CaCO_3$, Ca_3SiO_5 and Al_2O_3. TEM image reveals more precise particle size compared to that obtained from SEM/Gwyddion software and XRD. This work shows that the CSNPs can be produced, and they can be used as additives to coatings. Therefore, CS should not be left to waste as they are useful for additives in coatings.

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Author's Contribution

Funsho O. Kolawole: carried out literature survey on this present study, grinding and ball milling of cassava stem into nanoparticles, morphology study of the SEM images, interpretation of EDX and TEM results.

Johnson O. Agunsoye: Co-supervisor, review and correction of this present study and also the interpretation of SEM, EDX, XRD and TEM results.

Sefiu A. Bello: carried out analysis of particle size range using Gwyddion software from the SEM images, was also involved in the literature survey of this present study.

Jeleel A. Adebisi: sourced for cassava stems and prepared them, was also involved in the literature survey of this present study and interpretation of XRD result.

Suleiman B. Hassan: Lead Supervisor, involved in the review and correction of this present study and also the interpretation of SEM, EDX, XRD and TEM results.

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