



Featured Letter

Synthesis of coconut shell nanoparticles via a top down approach: Assessment of milling duration on the particle sizes and morphologies of coconut shell nanoparticles



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ABSTRACT

Coconut shell nanoparticles (CSNPs) were synthesised from coconut shell powders using a top down approach. Effects of milling time on the particle morphologies and sizes of CSNPs were studied. CS powders were milled for a maximum of 70 h using ceramic balls and a planetary mill. Milled samples taken at 16, 46 and 70 h were analysed using scanning electron microscope with attached energy dispersive X-ray spectrometer, X-ray diffractometer and UV–vis spectrophotometer. SEM micrographs revealed a difference in morphologies and appearances of the CSNPs. Particle size determination depicted a decrease in CSNPs' sizes with an increment in milling duration. The CSNP size determination from SEM aided with software and XRD aided with Scherrer's equation agrees with each other. This implies that the SEM observed CSNP sizes are in line with XRD crystalline sizes. The decrease in particles' Co K α X-ray absorbance with increment in milling duration is an indication of reduction in CSNPs' opaqueness. This agrees with fading of brownish colour of CS powders as the milling duration increased. The smaller the wavelength at which maximum absorbance of the Co K α X-ray occurred the smaller the CSNPs' sizes. Hence, an increase in surface area as the CSNPs' sizes decreased during milling led to particle agglomeration and formation of new compounds.

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1. Introduction

Coconut shell (CS) are naturally occurring structural components which form a protective chamber for coconut and its juice [1]. A coconut fruit contains three layers namely: endosperm, endocarp and mesocarp. The endosperm is the thick albuminous testa which is the white and fleshy edible part of the coconut fruit harbouring the coconut juice. The endocarp is the inner, hard lignocellulose composite known as coconut shell and the mesocarp is the ductile fibre-spongy husk called coir [2]. The coconut fruit is the product of coconut tree which was originated from South Asia. Now, it is found in South American and Africa [3]. It grows in tropical and rain forest climates. The coconut tree belongs to Plantae kingdom and Arecales order. Its tribe, genus and species are Cocoeae, Cocos and *C. nucifera* respectively; hence the botanical or binomial name *Cocos nucifera*. Coconut shells are agro

wastes from household and coconut processing industries when the edible parts of the coconut fruit have been removed.

Globally, many researches are now concentrating on agro wastes such coconut shell, palm kernel shell, banana peel, cashew shell, walnut shell, groundnut shell and others in order to have replacement for the high cost conventional glass and carbon reinforcements for metallic and polymer composite development which are structural composites for aircraft and automobiles [4–6]. The agro waste or natural fillers have advantages over conventional filler which includes low cost, high toughness, excellent specific strength and enhanced energy recovery.

Reports from many researches have proven to the fact that the mechanical milling/alloying otherwise called top down approaches are suitable techniques for the synthesis of nanoparticles or nanoalloy especially when the size of initial materials is within the micro-metre range. Synthesis of nanomaterials through mechanical milling depends on charge ratio, rate of rotation of vial, brittleness of materials, milling duration, size of the milling balls and materials of which the balls are made. These parameters dictate the size of the particles obtained from the milling process. However, milling time between 14 and 120 h have been reported

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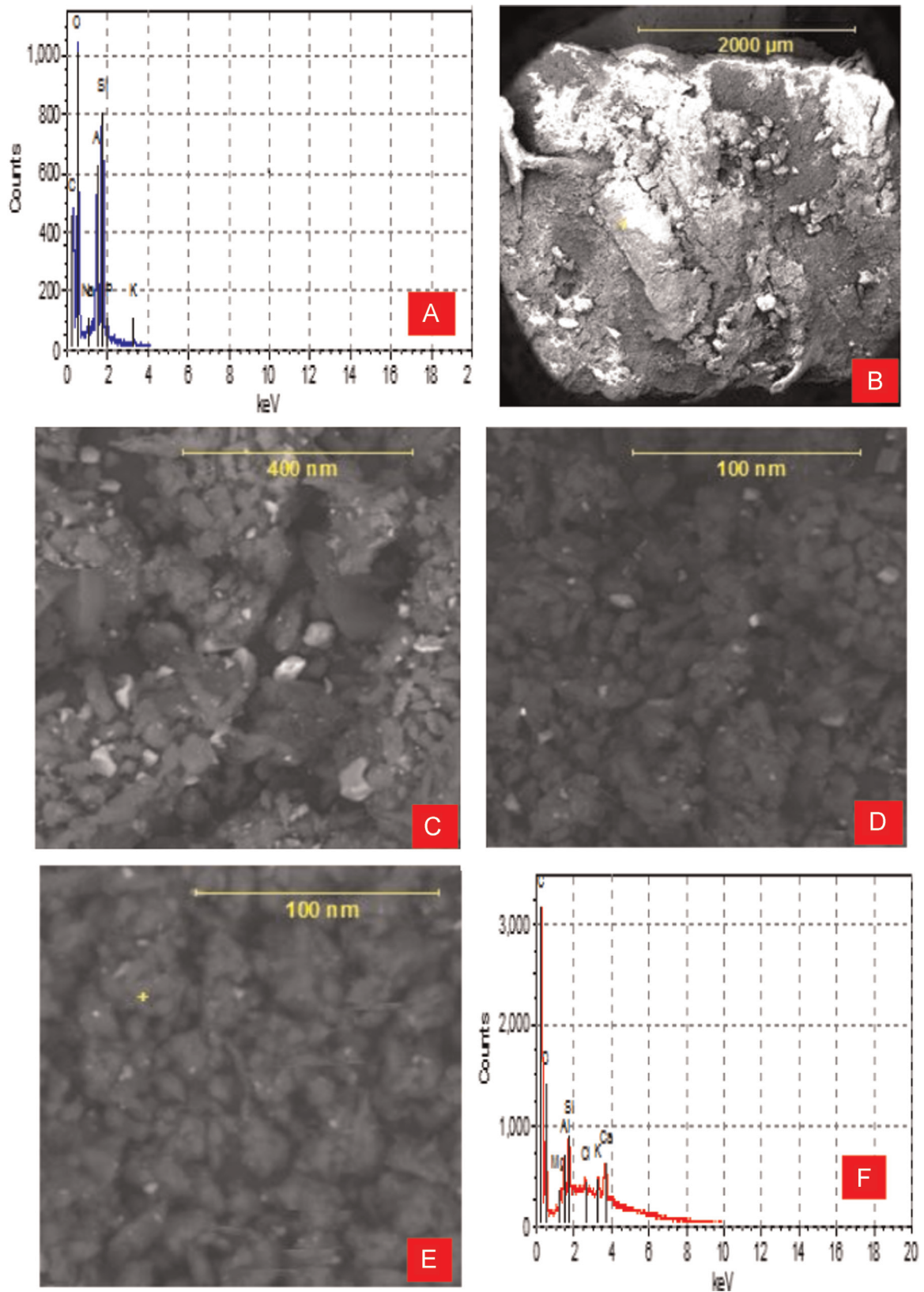


Fig. 1. (A) EDS of the bulk, (B) SEM of the bulk, (C) SEM of CSNPs at 16 hours, (D) SEM of CSNPs at 46 hour, (E) SEM of CSNPs at 70 hours millings and (F) EDS of CSNPs at 70 hours millings.

from different authors for nanoparticle synthesis [7–9]. In contrast to the background, processing of CSs at nanometric level is rare. Processing of CSs to obtain potential nanofillers will not only add

values to CSs but also lead to environmental cleanliness and wealth creation. However, in this work CSNPs have been synthesised using top down approach (mechanical milling). The

produced coconut shell nanoparticles can be used as natural nanofillers for the reinforcements of polymers and metals for green production of natural particle reinforced nanocomposites and nanoparticle-carburisation to harden the surface of materials for wear resistance application. The research work was aimed at studying the morphology and sizes of coconut shell nanoparticles (CSNPs) with respect to milling durations.

2. Materials and methods

CS powders (less than 37 μm size) used in this work were produced from the bulk CSs using a hardened steel crusher and a disc grinder. The scanning electron micrograph and proximate analysis of the bulk CSs are presented in Fig. 1A and B. The CS powders were milled for a maximum of 70 h at 5 h per day using a planetary ball mill, model: 87002 LIMOGES; type machine 28A2092 with mixture of ceramic balls of different sizes (5–60 mm). The milling was carried out at 10 charge ratios and the rate of revolution of the vial is 195. Samples taken at 16, 46 and 70 h were analysed using scanning electron microscope (SEM) with attached energy dispersive X-ray spectroscopy (EDS), ASPEX 3020; ultra violet–visible light (UV–vis) spectrophotometer, model JENWAY 6800 and a Panalytical Empyrean X-ray diffractometer with Pixcel detector. The slits were fixed with Fe filtered Co K α radiation. The phases were identified using X'Pert High score plus software; PAB-ICSD and ICDD (2014) databases. Samples were prepared using a zero background sample holder. Sizes of CSNPs were determined using SEM/software and XRD/Scherrer's equation (Eq. (1)) [10–14].

$$\text{Mean crystallite size} = \frac{\lambda K}{\beta \cos \theta} \quad (1)$$

where K is the shape factor (0.9 assuming Gaussian function to fit the peak); λ is the X-ray wavelength; β is the full width half-maximum (in Rad) and θ is the light scattering angle.

3. Results

CSNPs have different sizes and morphologies as the milling duration increased (Fig. 1C–E). Many CSNPs formed networks of agglomeration with few individual particles appeared alone. Decrease in particle size with an increment in milling durations led to an increase in surface area (high surface energy) of the CSNPs. Physical and chemical interactions among extremely fine particles are responsible for particle agglomeration (due to cold welding) and formation of new compounds (Fig. 2A–D). The broadening of X-ray spectrum peaks in Fig. 2B–D is an indication of a decrease in particle size as the milling duration increased. However, in Fig. 2A major peaks occurred at diffraction angles (2θ) of 25.43 and 40.07° respectively. Phases at these peaks are $\text{C}_2\text{H}_8\text{Cl}_1\text{N}$ and SiO_2 with respective inter-planar spacing of 4.07 and 2.59 Å. In Fig. 2B, three major peaks were identified at 31.07, 33.32 and 36.12°. The corresponding phases are SiO_2 , NaNO_3 and C_2CaMgO_6 with respective inter-planar spacing of 3.34, 3.12 and 2.28 Å. Fig. 2C reveals that phases at the major peaks are SiO_2 and CaMgC_2O_6 with inter-planar spacing of 3.35 and 2.89 Å respectively. This occurred at respective diffracting angles of 30.98 and 36.04°. Phases indicated in Fig. 2D are SiO_2 and C_2CaMgO_6 with inter-planar spacing of 3.85 and 2.89 Å at diffracting angles 30.95 and 36.02° respectively. Peak representing each phase is indicated by vertical

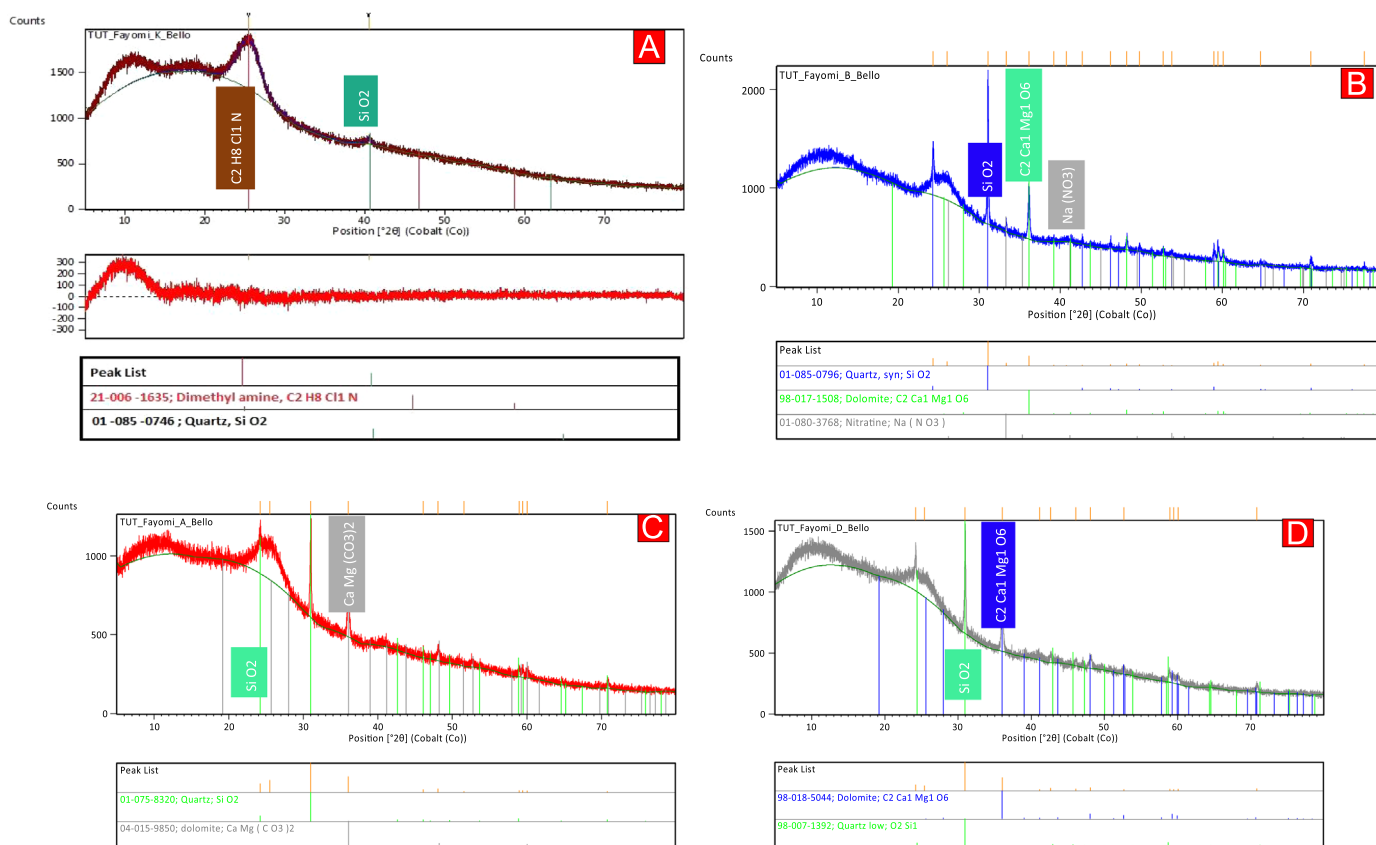


Fig. 2. XRD: (A) CS powders, (B) CSNPs at 16 h, (C) CSNPs at 46 h and (D) CSNPs at 70 h.

lines painted in different colours for the purpose of phase identification. The difference in inter-planar spacing is attributable to severe plastic deformation taking place during the ball milling process. EDS proximate analysis of the CSNPs obtained at 70 h milling revealed higher carbon count score with corresponding reduction in the oxygen count score than those of bulk CS (Fig. 1F and A). This change is attributed to dryness of the CSNPs with an increment in milling duration. The particle breakage is a function of the shocks or impacts received by the particles from the milling balls. During the impacts, kinetic energy transferred by the milling balls to the particles was transformed into heat energy which raised the temperatures of the CSNPs. The heating effect led to evaporation of the moisture contents of the CS particles. This made the particles more brittle and enhanced their breakage tendency but on the other hand, resulted in particle softening/gummy leading to particle agglomeration. Presence of calcium and

magnesium may be due to contamination from the milling balls and the vial's inner wall. The particle size determination from SEM aided with software revealed maximum sizes of 281.4, 170.01 and 154.03 nm; minimum sizes of 6.85, 4.09 and 4.52 nm and average sizes of 119.2 ± 0.85 , 72.1 ± 0.22 and 49.84 ± 0.48 nm at 16, 46 and 70 h milling respectively. Particle size determination from XRD depicted maximum sizes of 279.24, 168.69 and 153.85 nm; minimum sizes of 6.19, 3.47 and 4.32 nm and average sizes of 118.95, 71.78 and 49.85 nm at 16, 46 and 70 h milling respectively. This indicates reduction in particle sizes with an increase in the milling duration. However, the CSNP size determination from both equipment agrees with each other (see Fig. 4A and B). This implies that the SEM observed CSNP sizes are in line with XRD crystalline sizes. The decrease in amount of light absorbed (absorbance) by CSNPs with an increment in milling hour is attributable to fading of deep brownish colour of the CS powders (Fig. 3A–C). This is an

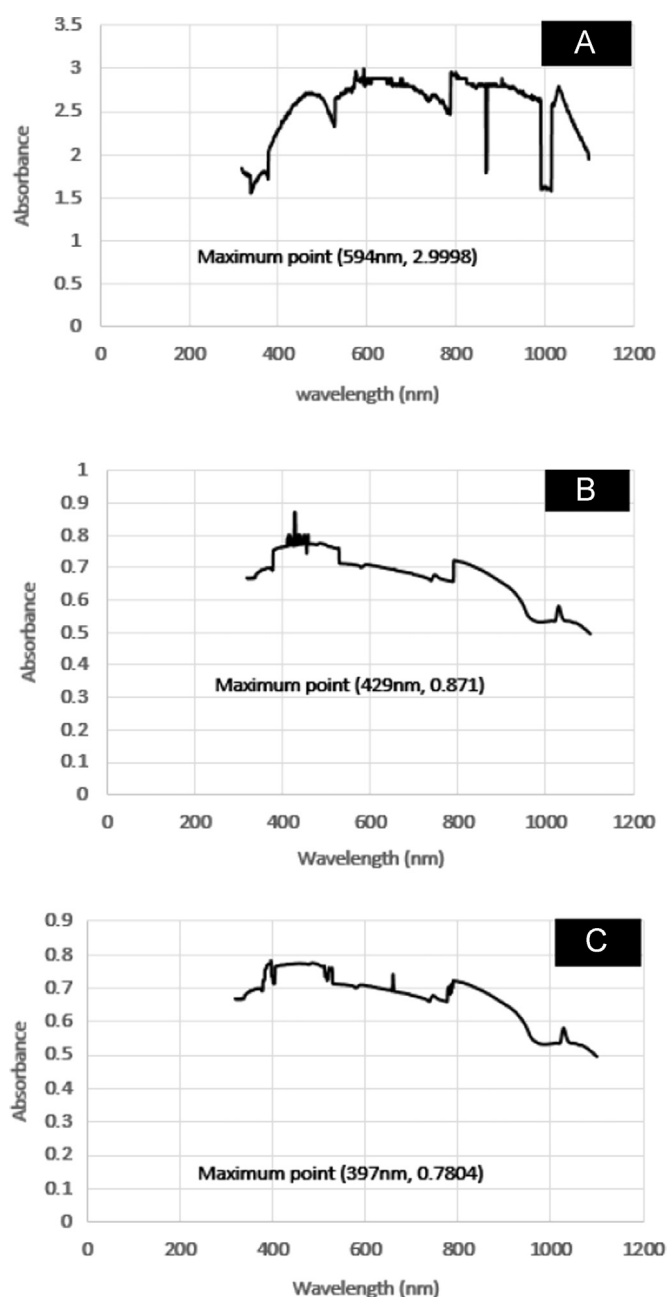


Fig. 3. UV-vis spectra (A) CSNPs at 16 h, (B) CSNPs at 46 h and (C) CSNPs at 70 h.

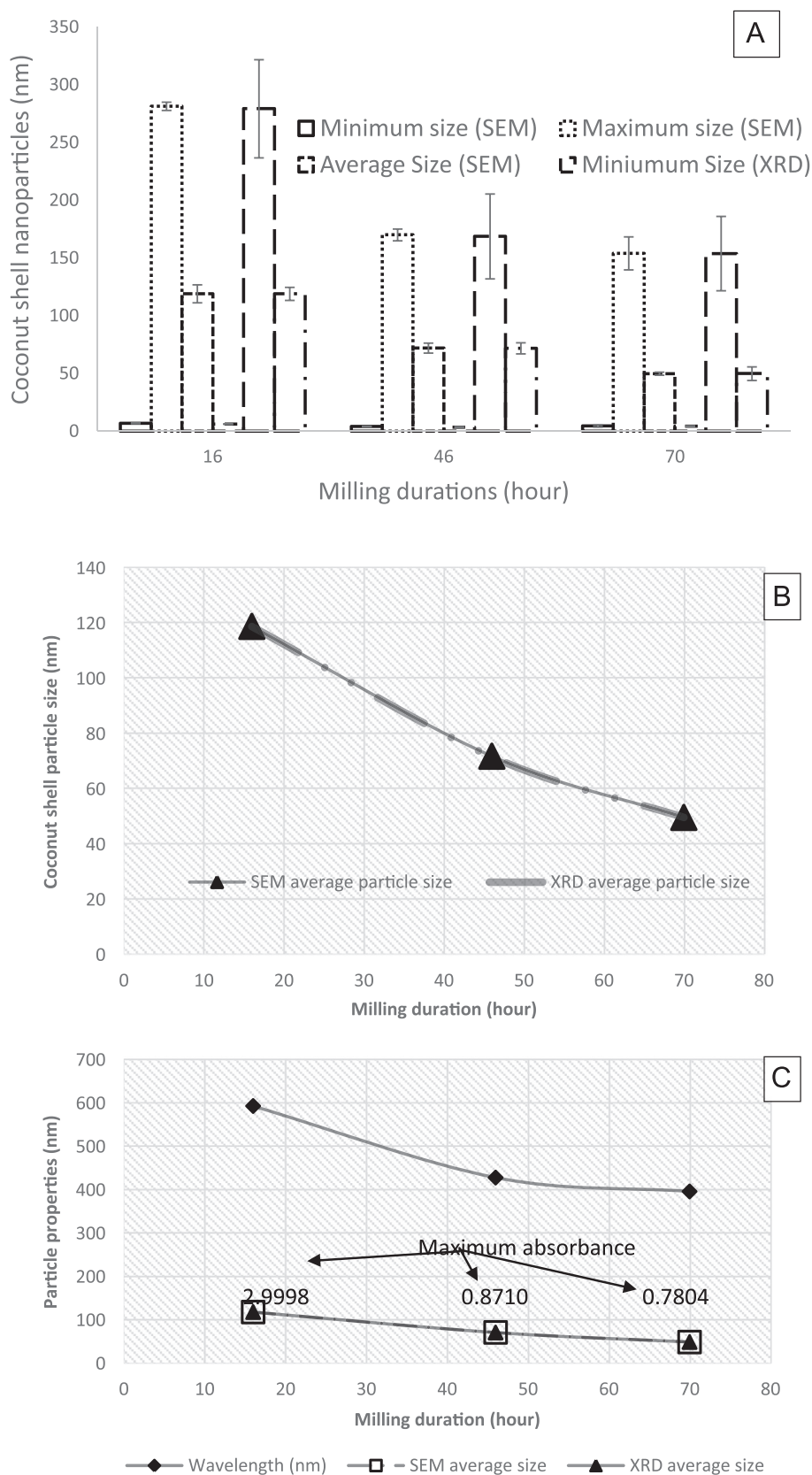


Fig. 4. Properties of CSNPs (A) SEM/XRD CSNP sizes, (B) average CSNP sizes and (C) CSNP sizes and absorbed X-ray wavelength with milling duration.

indication of a decrease in the opaqueness of the CSNPs. There is a reduction in wavelength of Co K α X-ray (at maximum absorbance) with increment in milling duration (Fig. 4C). This indicates a

reduction in the size of the CSNPs. The smaller the particles, the greater are their tendencies to scatter or absorb X-ray of extremely small (nano) wavelength. This agrees with Raleigh's distinction

between nanoparticles and big particles with respect to X-ray's wavelength [15,16].

4. Summary and conclusion

Summarily, synthesis of coconut shell nanoparticles through mechanical milling was achieved. The size of the CSNPs decreased with an increment in the milling duration. Formation of new phases such as C_2MgO_6 is attributable to high surface energy of the CSNPs leading to chemical combination of the phases present in the particles. Absorption of X-ray of extremely low wavelengths by CSNPs is an indication of their extremely small sizes. The synthesised CSNPs can be used as low cost natural nanoparticles for metal and polymer reinforcements for green production of nanocomposites. It can also be used in nanoparticle-carburisation to impart hard case to materials for wear resistance applications.

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References

- [1] S.A. Bello, Ph.D. Seminar 1 Dissertation, Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria, 2015, p. 82.
- [2] J. Sarki, S.B. Hassan, V.S. Aigbodion, J.E. Oghenevweta, *Alloy. Compd.* 509 (2011) 2381.
- [3] J.T. Alberto, Doctoral Thesis, Stockholm, Sweden, 2008, p. 83.
- [4] S. Faye, S. Graham, H. Alan, K. Ajay, Q. Robert, The Inter-Agency Group Composite, United Kingdom, 2009.
- [5] S.B. Hassan, J.E. Oghenevweta, G.B. Nyior, V.S. Aigbodion, The effect of vacuum carbonisation of waste maize stalk on the thermal resistance of polyester/maize stalk particulate composites, *Plast. Polym. Technol. (PAPT)* 2 (3) (2013) 68–74.
- [6] E.Y. Ishidi, E.G. Kolawole, I.K. Adamu, C.M. Obele, *JETEAS* 2 (6) (2011) 934.
- [7] T.P. Yadav, R.M. Yadav, D.P. Singh, *Mech. Milling: Nanosci. Nanotechnol.* 2 (2012) (2012) 22.
- [8] J. Raphael, G. Daniel, *Prog. Mater. Sci.* 50 (2005) 92.
- [9] M. Razavi, M.R. Rahimpour, R. Yazdani-Rad, *Alloy. Compd.* 509 (2011) 6683.
- [10] 02_Basic Xrd.pdf.
- [11] 17_Xray-Diff.pdf.
- [12] R. Ellingson, M. Heben, X-ray Diffraction and Crystal Structure, PV Materials and Device Physics Lab, University of Toledo, 2011, p. 1–20.
- [13] M. Birkholz, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (001_Kapitel).
- [14] S.A. Speakman, Center for MSE, MIT (<http://prism.mit.edu/xray>).
- [15] J.L. Taylor, C. Lynch, J.F. Dlugos, *UV/Visible Spectroscopy*, USA Perkin Elmer, Inc., 2013, p 1–11.
- [16] D. Chamberlin, R. Trutna, *Physics of Particle Size Spectrophotometry*, USA Agilent Technologies, Inc., 2008, p 1–8.