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Production, Characterization and Prospect Applications of Coal Nanoparticles

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Abstract

Coal ash is a waste material produced by combustion of coal in a thermal power station, In this paper, an attempt has been made to modify the micro sized coal ash into nano structured coal ash using High Energy Ball Milling. The smooth, glassy and an inert surface of the coal ash can be altered to a rough and more reactive state by this technique. Ball milling was carried out for the total duration of 30hrs. The sample was taken out after every 10 hours of milling for characterizing. The nanostructure coal ash was characterized for its crystallite size, using X-Ray diffractometer. It was found that after 30 hrs of milling, percentage crystallite size of quartz phase present in the coal ash was reduced from 63% to 37% for fresh coal ash and 30hr ball milled powder respectively, thus increasing the amorphous domains in it. The size, shape and texture of the fresh as well as nano structured coal ash were studied using Scanning Electron Microscopy (SEM). The fresh coal ash particles were found to be spherical in shape, while the shape of the 30hrs milled particles was found to be irregular and the surface morphology was also rough.

Keywords: Coal Ash; High Energy Ball milling; Nanomaterial; carbon nanoparticles; XRD- analysis; Electron Microscopy.

1.0 Introduction

Carbon-based nanomaterials have attracted great interest in recent decades. Understanding their properties and exploring their promising application have led to an explosion of research worldwide. In particular, carbon nanoparticles have attracted much attention due to their significant role in different fields, from arc generated soot and vacuum deposited thin films to interstellar dust [1]. One type of carbon nanoparticles, carbon black, has been widely used as filler in rubber, dye in paint, and catalyst carrier in chemistry for centuries. Potential newly found applications of carbon nanoparticles occur in such diverse areas as protective coatings, electronic devices, field emission devices, super capacitors, micro sensor preconcentrators, and nonlinear optical devices, further prompting more intensive research [2]. A variety of ways have been reported to synthesize nano level materials such as plasma arcing, chemical vapor deposition, electro deposition, sol-gel synthesis, flame combustion (pyrolysis) high energy ball milling etc. These methods have been used successfully to prepare carbon nanoparticles in different ambient. Among these methods high energy ball milling has advantages of being simple, relatively inexpensive to produce, applicable to any class of materials and can be easily scaled up to large quantities[2]. In this mechanical treatment, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the balls and the powder. This produces novel crystalline and amorphous materials with crystallite sizes at the nanometer scale[3]. More research in this area is clearly needed to fully explore the possibilities offered by these materials. In this work an attempt has been made to modify the coal ash by transforming the micro sized coal ash into nano structured coal ash using high energy ball milling. The smooth, glassy and an inert surface of the coal ash can be altered to a rough and more reactive state by this technique [4].

2.0 Experimental Procedure

2.1 Preparation of The Coal Sample Material for High Energy Ball Milling

The coal ash material which was obtained from Oji- River power station was washed in distilled water and the carbon that

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creamed up during washing was removed. It was then dried at 100 ºC for 5 hrs to remove water. Dried coal material was sieved using British Standard Sieve (BSS). Coal sample material fractions that passed through mesh no. 170, but got retained on mesh no. 240 were collected and magnetic separation was carried out to remove the magnetic impurities. Then the sample was taken for ball milling.

2.2 High Energy Ball Milling

The reduction in particle size of the coal ash from micron level to the nano level was carried out using a high-energy ball milling machine in a stainless steel chamber of capacity 5kg/hr using metal balls of0.21 m sizes respectively. The total duration of milling was 30hrs. The rotation speed of the planet carrier was 82 rpm. The milled sample powder was taken out at a regular interval of every 10hrs of milling. Then this milled powder was dried in an oven at 80^0C for 2hrs. This dried powder was then taken for characterization. The high energy ball milling was done at the material and metallurgical laboratory department, Federal University of Technology Owerri (FUTO) Imo state.

3.0 Results and Discussion

3.1 Morphology Studies with (SEM)

A Scanning Electron Microscope (SEM) was used to evaluate the texture, morphology and elemental composition of fresh and ball milled coal ashes. The images were taken at suitable accelerating voltages for the best possible resolution using secondary electron imaging.

The size, shape and texture of the fresh coal ash as well as nanostructure coal ash were studied using Secondary Electron Imaging mode of Scanning Electron Microscopy (SEM). Figure 1 shows the SEM image of fresh coal ash, from the SEM image, it can be observed that the fresh coal ash particles are mostly spherical in shape. This is as a result of the combustion temperature and cooling rate in the thermal power plant[5]. Figure2 shows the SEM image of 10hrs ball milled coal ash. Here the spherical structure of fresh coal ash has been destroyed, this is as a result of the cold welding condition the material was subjected to, and hence the particles appear like enlarged flakes [6]. These large flake shaped particles are further crushed by intense impacts of the balls, hence the decrease in particle size occurs with increasing milling time as shown in Figure3, and figure 4 the SEM images for 20hrs, and 30hrs, ball milled samples of which the structural breaks is more.It can also be observe that at these respective times, the shape of the particles became irregular and the surface morphology became rough, which makes them more compatible with various metallic and polymeric matrices, resulting to a more beneficial application such as particulate nano filler in polymeric or metallic matrices[7].

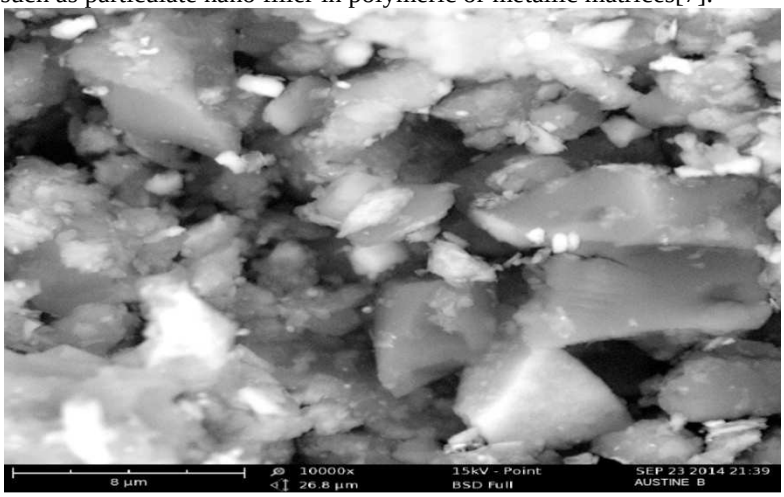

Figure 1: The SEM image of fresh coal ash. The fresh coal ash particles are mostly spherical in shape.

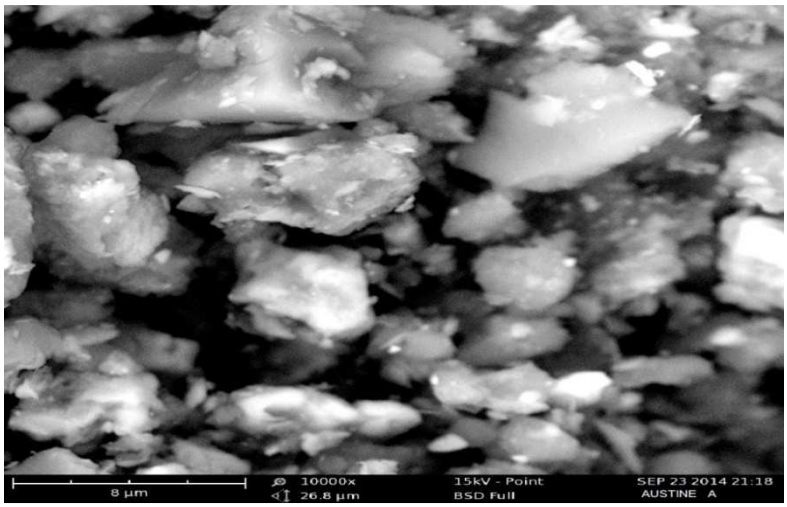

Fig 2: The SEM image of 10hrs ball milled coal ash. Here the spherical structure of fresh coal ash has been destroyed.

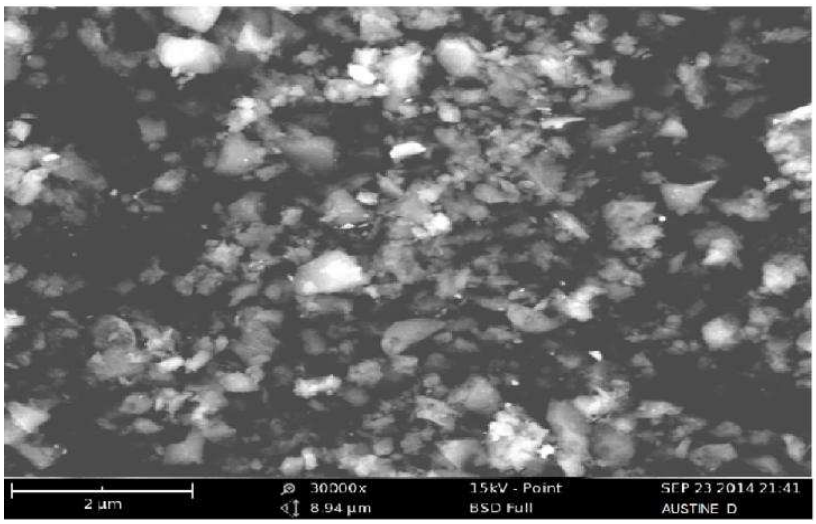

Fig 3: The SEM images for 20hrs, ball milled samples of which the structural breaks is more.

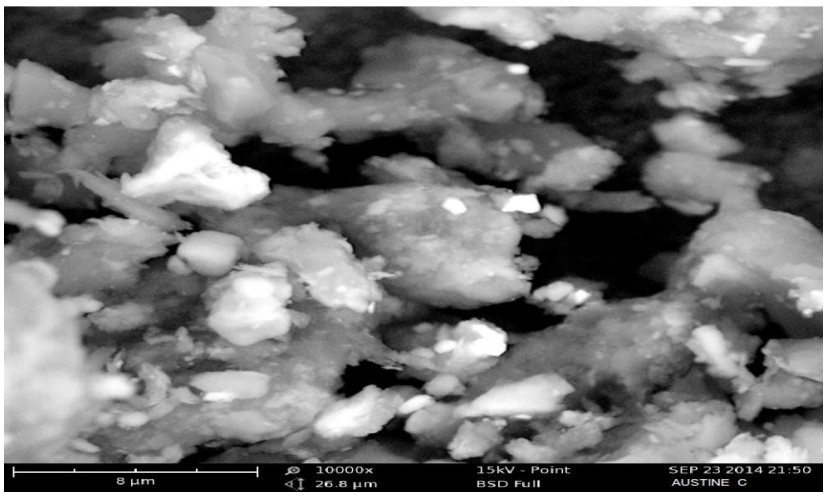

Fig 4: The SEM images for 30hrs, ball milled samples of which the structural breaks is more and rough.

3.2 X-Ray Diffractometer (XRD) Result

X-ray diffraction measurements were carried out to investigate the structural changes and phase transformations of coal powders that occurred during mechanical milling. The X-ray diffraction measurements were carried out with the help of a Goniometer model PW3050/60using Cu Kα radiation (λ = 1.54060 Å) at an accelerating voltage of 40 kV and a current of 30 mA. The samples were scanned in the range from 20 to 900 in the 2θ range and analyzed for crystallite size, peak height, and crystallinity.

The X-ray diffraction (XRD) pattern of fresh coal ash as well as the ball milled ash is shown in Figures 5, 6, 7, and 8, which show the phases present in the fresh coal ash as well as the ball mill coal ash for 10hrs, 20hrs, and 30hrs respectively. These phases are largely quartz (Silica (SiO_2)), which is the major phase, kaolinite (Al_2 $si2O_5.(OH)_4$), and calcite ($CaCo_3$). Also their strongest peaks as well as their d-spacing values can equally be seen from the diagrams. Quartz phases exhibits strong peaks at 26.6467^0, 26.6210^0, 26.6240^0, and 26.6000^0 2-theta values and corresponding (d-spacing) of 3.34540, 3.34580, 3.34540, and 3.34840(A^0), for each of fresh, 10hr, 20hr and 30hr milling respectively. The kaolinite phase shows strong peaks at 20.8830^0, 24.8440^0, 24.8440^0, and 24.8730^0 2-theta values and corresponding (d spacing) of 4.2538, 3.5809, 3.5809, and 3.5768 (A^0). For each of fresh, 10hrs, 20hrs and 30hrs milling respectively. Also the calcite phase shows a peak at 29.3950^0, 29.3900^0, and 29.3900^0 2-theta values and corresponding (d spacing) of 3.0361, 3.0366, and 3.0366 (A^0) for each of 10hrs, 20hrs and 30hrs milling respectively. A close observation on the XRD pattern of the various coal samples show that The quartz Silica (SiO_2) phase is the maximum sufferer during milling, hence with increasing the milling time SiO_2 peaks shifts slightly to the lower angels and also broadening of the diffraction pattern occurs leading to an increase in lattice strain with increase in milling time, this is because during ball milling the intense mechanical deformation experienced bythe coal ash powder leads to generation of lattice strains, crystal defects and this plus the balance between cold welding and fracturing operations among the powder particles is expected to affect the structural changes in the powder[8].

The average crystallite size was determined by the Full Width at Half Maximum (FWHM) of the X-ray diffraction peak using Scherrer's equation

$t = k\,\lambda/\beta\cos\theta$(1)

Where t is the particle diameter, λ is the X-Ray wavelength, β is the FWHM of the diffraction peak, θ is the diffraction angle and k is the Scherrer's constant of the order of unity for usual crystals. Figure9 illustrates the variation in percentage crystallite size of the coal ash with the milling time. A close look at the graph shows a steady decrease in the percentage crystallite size of quartz phase present in the coal samples which got reduced from 63% to 37% for 30hrs milling time. The measurement of crystallite size in the mechanically milled powders is very important since the phase constitution and transformation characteristics appear to be critically depending on them[8].

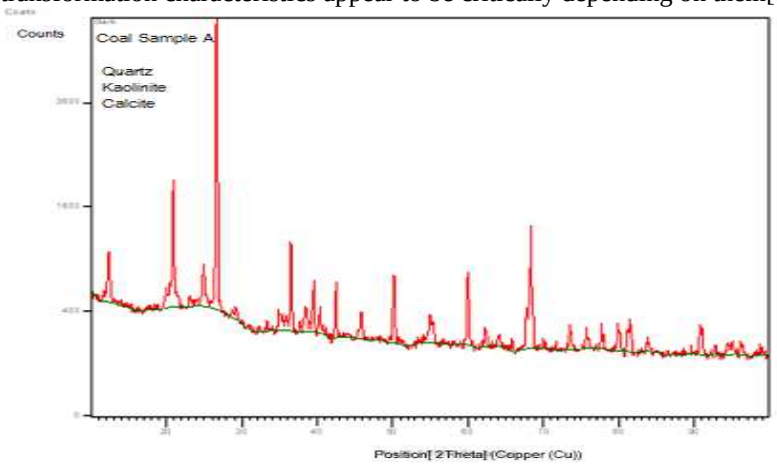

Fig 5: The X-ray diffraction (XRD) pattern of fresh coal ash, showing the phases present, their respective peaks, and d-spacing (A^0).

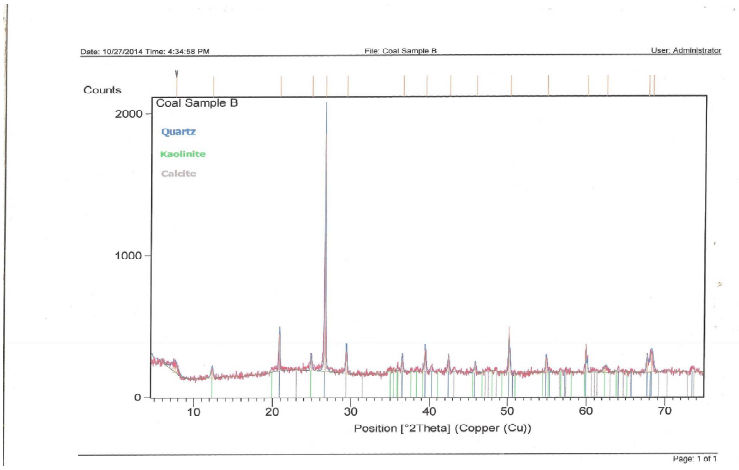

Fig 6: The X-ray Diffraction (XRD) pattern of 10hrs ball milled ash, showing the phases present, their respective peaks and d-spacing (A^0)

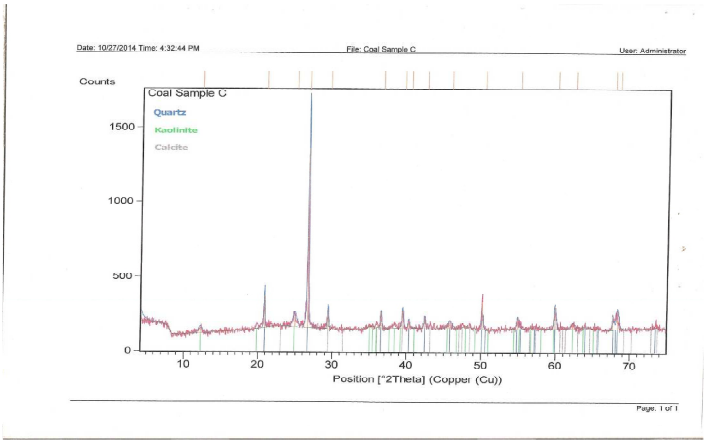

Fig 7: The X-ray Diffraction (XRD) pattern of 20hrs ball milled ash, showing the phases present, their respective peaks and d-spacing (A^0)

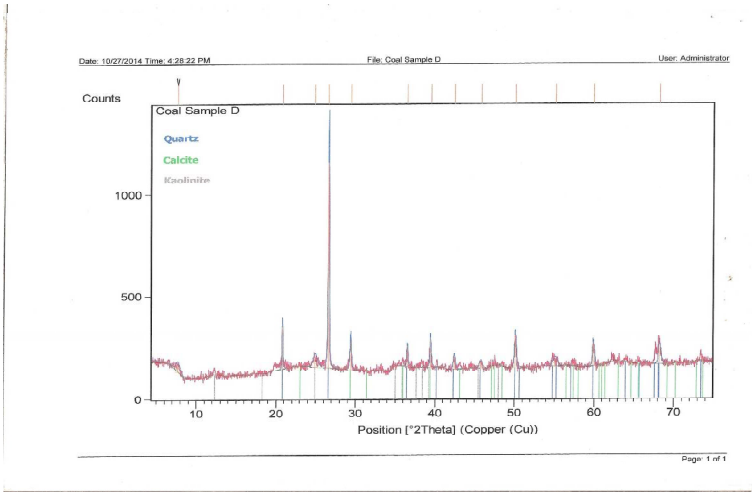

Fig 8: The X-ray Diffraction (XRD) pattern of 30hrs ball milled ash, showing the phases present, their respective peaks and d-spacing (A^0)

3.3 Crystallinity

Crystallinity refers to the degree of structural order in a solid. Crystallinity is usually specified as a percentage of the volume of the material that is crystalline [8]. The decrease in crystallinity of fresh coal ash with ball milling hours is shown in Figure9. This decrease was observed from 63% to 37% for fresh coal ash and 30hr ball milled powder respectively. Looking at the graph, we can see that increasing the milling time decreases the crystallinity of the coal ash, thus increasing the amorphous domains in it[8]. This change is beneficial for the applications such as particulate nano filler in polymeric or metallic matrices. The enhanced amorphous content is very encouraging as it may lead to better compatibility with various metallic and polymeric matrices.

Table1:%Crystallite size of quartz phase in fresh and ball milled coal ash.

% Crystallinity	Milling time
63	0
52	10
48	20
37	30

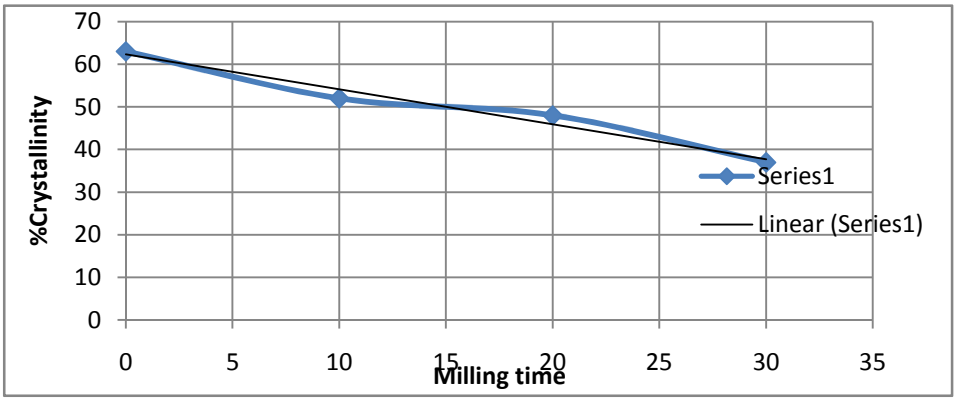

Fig 9: Variation in crystallite size of the coal ash with the milling time.

4.0 Conclusion

The size reduction of coal ash from micrometer level to nano meter levels has been achieved by high energy ball milling for theperiod of 30 hrs. The coal ash becomes more amorphous and the process equally converts the surface into rough and reactive one. The lattice strain was increased with increasing the milling time. The coal ash has become more amorphous and the crystallite size of the quartz phase has been reduced drastically. The spherical shape and smooth surface texture of the coal ash have been changed into irregular shape and rough surface by ball milling which is evidenced from SEM studies.

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