International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.3, pp 1465-1473, 2014-2015

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Structural and Morphological study of Carbon Nanoparticles synthesized using Oxidation, Thermal decomposition and Solvo chemical methods

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Abstract : Isotopes of elemental carbon play a major role in material engineering due to its distinct electrical, mechanical and optical properties that various for different isotopes of carbon. Carbon nanoparticles on the other hand have tuneable fluorescent property used for bio imaging and drug delivery applications. Carbon based quantum dots are less toxic and more bio compactable compared to another nanomaterials.The carbon nanoparticles of few nanometers are used for imaging due to its prominent emission in visible region where as excited in IR region thus these nanoparticles are suitable for imaging without disturbing the nearby tissue. But mechanism of fluorescence is still not clear. This work is aimed to study the structure and morphology of carbon nanoparticles synthesized with different methods. There are many approaches to obtain carbon nanoparticles such as high energy ion beam irradiation, laser ablation of graphite, thermal decomposition of organic compounds, electro oxidation of graphite, oxidation of carbon soot, Solvo chemical etc. The nanoparticles synthesized from the above method shows different fluorescence depends on their method of synthesis. The synthesis of carbon nanoparticles is made using oxidation, thermal decomposition and solvo chemical methods and the structure and morphology of these nanoparticles were studied for different surface modifiers and carbon sources. The Nano particles synthesized from each method is characterized by Fourier Transform Infra-Red spectroscopy (FTIR) and UV-Visible Spectroscopy (UV-VIS), Scanning electron microscopy (SEM).

Keywords: Structural and Morphological study, Carbon Nanoparticles, Oxidation, Thermal decomposition, Solvo chemical methods.

Introduction:

Carbon-based nanomaterial's also called as Carbonaceous nanomaterial's. Carbon-based nanomaterial's are the most researched materials of the 21st century with an international intention of growing industrial quantities due to their unique properties. Carbon materials which include carbon nanotubes, fullerenes, carbon nanodots ,nanofibers, diamonds, graphenenanosheets, and graphene onionsetc., have generated immense research interest in the recent past owing to their excellent physical,thermal,chemical, optical ,electronic properties, bio compatibility and excellent corrosion resistance. These materials have shown promising applications in nanotechnology, polymer composites, electrochemical energy storage and conversion, filtration, hydrogen storage, catalysis and biotechnology, bio sensing, bio imaging, electrochemistry, drug delivery, photo & chemical stability, tuneablephotoluminescence(PL)and catalysis applications. Successful utilization of carbon nanoparticles in various applications is strongly dependent on the development of simple, efficient and inexpensive technology for its production. Approaches to synthesizing carbon nano particles can be classified into two main groups: top-down and bottom-up methods. The top-down methods are primarily based on the post treatment of nanocarbon exfoliated from various larger carbon structures[1-8].the bottom-up approaches consist of thermal decomposition of suitable molecular precursors[9-18],dehydration of carbon hydrates using concentrated sulphuric acid and the supported synthetic method[20,21]. In general, these carbon nanoparticles have been synthesized using various synthetic processes including thermal carbonization, laser irradiation, sonication, and exfoliation[22-24]. Many methods such as chemical oxidation of soot,laser ablation of carbon, electrochemical oxidation of graphite and incomplete thermal decomposition of ammonium citrate salts have been developed to prepare carbon nanoparticles which have potential applications in bio-imaging, light-emitting diodes, metal ion detection,temperature probes, and intercellular pH sensing. However, the lack of thorough understanding of the PL mechanism, has hampered wider applications. Infact, PL from Carbon nano dots which tend to be over simplified in many studies is excitation dependent. There are few reports that the carbon nanoparticles alone, like traditional semiconductor quantum dots, showed photo catalytic activity. Although the composites of carbon nanoparticles and other inorganic materials have shown good photo catalysis performance, it is believed that carbon nanoparticles acted only as visible light sensitizers in the photo catalytic process[25].Carbon nano particles are also synthetized by solvothermal method of pyrolysis organic materials. For example, glucose as the carbon source and glycol as solvent heat up to 180^{0}C. Then, the product emits fluorescence weakly, which needs further passivation[26]. Photo luminescent Carbon nano particles also extend to carbon nanoparticles separated from candle soot, but this combination has a very low photoluminescence[27]. Recently, it was discovered that Carbon nano particles were synthesized from natural materials such as juice and lignin and so on[28]. It indicates that is possible to synthesize Carbon nano particles from two or more kinds of carbon source. The advantage of this method is that it can elevate fluorescence intensity of Carbon nano particles and doesn't need passivation. Candle soot originated carbon nanoparticles (CNPs) have been rediscovered as a new class of carbonaceous nanostructures with interesting properties. These studies indicated that candle soot can be used as starting material for the preparation of Carbon nanoparticles. Synthesis of carbon nanoparticles with controlled microstructures is possible through chemical modification and alteration of the processing parameters. Among the various carbon allotropes, particulate nanostructures receive more attention due to their versatility in fabrication and their extensive applications in polymer Nano composites as Nano fillers, waste-water treatment, biomedical imaging, optical devices ,polymer composites, electrochemical energy storage and conversion, catalysis, filtration, hydrogen storage, and biotechnology .One of the key factors in controlling the morphology and the yield of the carbon nanoparticles is the precursor material. Various carbon precursors such as graphite powders, petroleum pitch, carbon rich polymers, and other kinds of liquid/gaseous hydrocarbons have been extensively used for the fabrication of carbon nanoparticles. However, there is a need for alternate carbon sources for the synthesis of carbonaceous materials due to increasing oil prices, depleting petroleum resources, their negative environmental impacts, and increasing demand for carbon-based nanomaterials in various emerging fields. Hence, renewable carbon resources such as plant biomasses, bio based oils, and hydrocarbons have been explored for the fabrication of carbon nanostructures. In this contribution we describe an effective method to produce carbon nanoparticles at ambient temperature from different precursor and using various methods like sol-gel, hydrothermal and hydrolysis process[29]. Then the prepared samples are subjected to various characterization like SEM,XRD,UV/VIS Spectroscopy,FTIR Spectroscopy And the carbon nanoparticles samples are further extensively studied for photo catalytic activity, Photoluminescent-flurocent properties etc., for future applications.

Experimental part:

Carbon from candle:

Synthesis of carbon is made using candelas in this method. 30cm height of stainless steel box is taken and polished .hard candles are placed inside the box ,pores are made in one of the face of the stainless steel box to escape air .candles are ignited inside the box waited till the candles are completely burnt .after the candles are burnt completely the top of the box is removed separately. We can find that top of the box was coated with carbon particles, using sterilised spatula the entire surface of the top plate is scratched and black residue is collected.

Carbon from coconut shell:

Carbon can be obtained from burning anything which formed naturally. Here we are using empty coconut shells to extract the carbon from it, we took few empty coconut shells and made them burn under high heat using Bunsen burner .after the shell is completely burnt it appears dark ,using hammer break it into small pieces .the small pieces are collected and crushed using mortar and the particles are collected.

Carbon from coconut husk:

Here we collected the carbon by simply heating coconut husk using the burner and after the husk is burnt completely, the burnt coconut husk is made into pieces and crushed using mortar and residue is collected.

Carbon using Orange Juice:

Few oranges are taken and peeled off and juice is extracted (70ml) .the orange juice is filtered using filter paper. The juice is poured into a Teflon coated autoclave and kept in muffle furnace at 120^c for 2.5 hours .the temperature of the muffle furnace is set in a rate of 15minutes .after 2.5 hours the sample is taken out and waited till the autoclave comes to room temperature .then the sample is taken out in a 100ml beaker ,the orange juice is turned in black liquid from orange colour ,this show the presence of carbon .then the sample is subjected to centrifuge at 5000rpm un till all the sample is done. Then the residue is taken and dried at 50^c for 2 hours .then the sample is collected.

Carbon using Acids:

In order to get carbon nano particles .we need a carbon source to start with. Here we use a carbon rich material called sugar .sugar is a carbon material thus we use it as carbon source , using acids like hydro chloric acid(HCL),sulphuric acid(H_2SO_4) and nitric acid(HNO_3) we synthesis carbon particles .

Carbon particles using Hydro chloric acid (HCL):

To synthesis a carbon particle using HCL we need few grams of sugar since we use it as carbon source and few mille litters of acid. Here we take 7.2 grams of pure sugar poured in a 100ml beaker along with 50ml of distilled water. start stirring using magnetic stirrer till the sugar is dissolved .after the sugar in the beaker is completely dissolved by using filter paper filter the liquid ,after filtering add 50ml of con.hydro chloric acid in to the beaker of sugar solution .place the beaker in a liquid sonicator bath and start sonication process for 4 hours continuously .we can observe colour change for each stipulated time ,for first 30 minutes it turned orangish yellow from transparent liquid then after 1 hour it turned brown after 2 hours it turned black which indicates formation of carbon particles .after the sonication process is done the sample is taken out in a beaker and certification is done at 5000rpm till the sample in the beaker is over .then the residue is collected and dried in a Petridis at 50^c for 2 hours ,then the sample is collected.

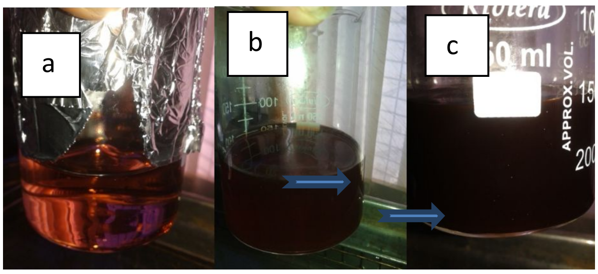


Figure 1:a,b&c are the change in colour in sample during a time interval of 1 hour

Results and discussion:

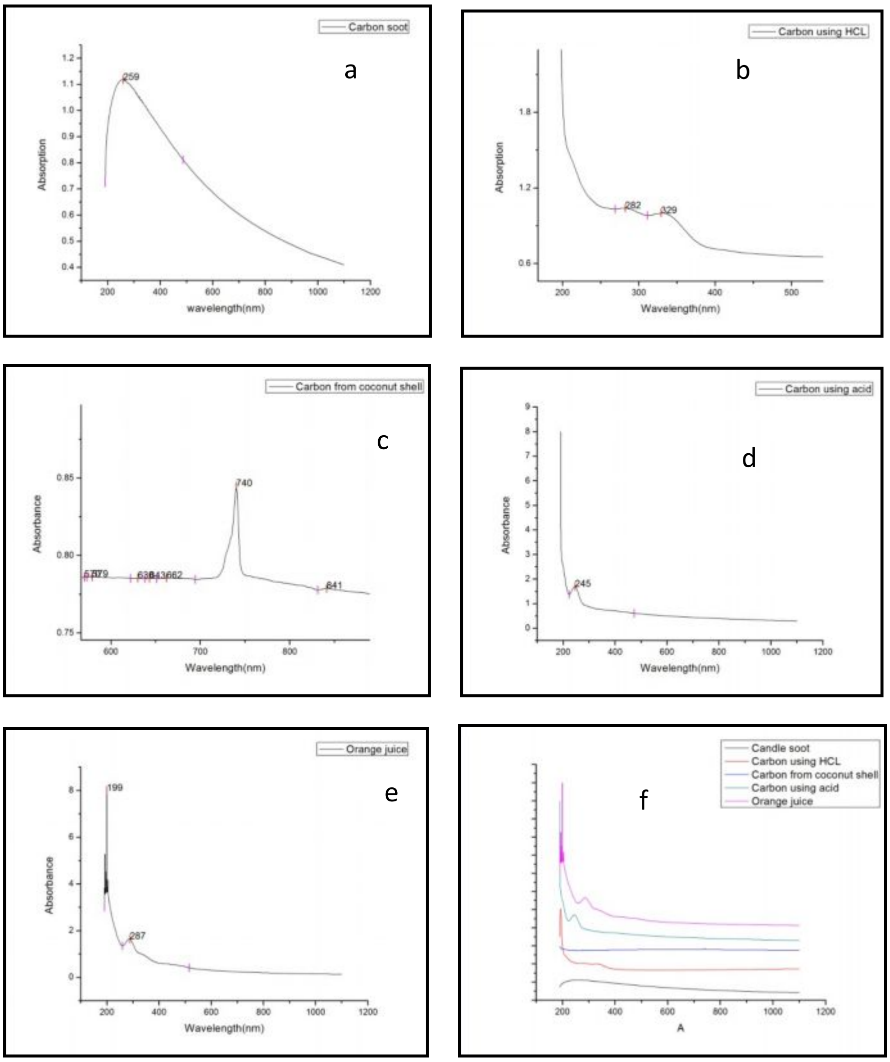
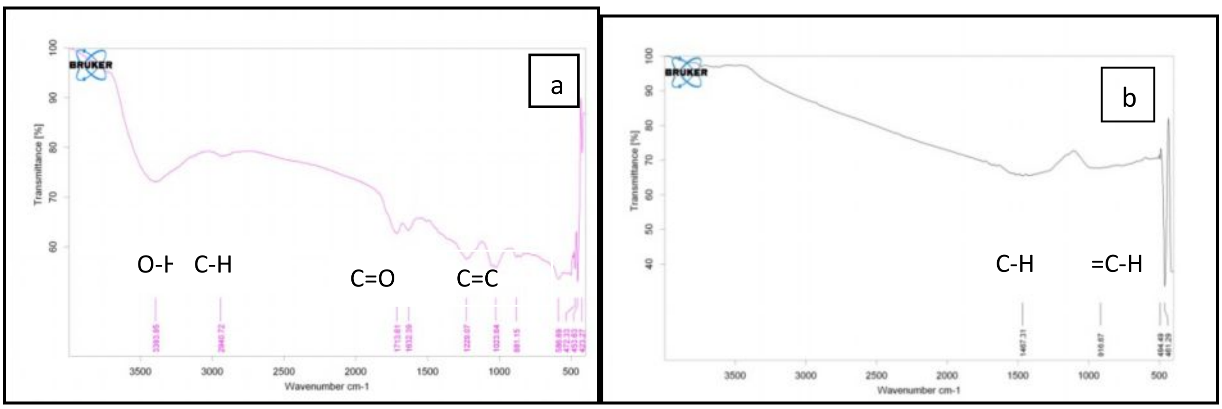


Figure 1: It shows UV-VIS absorption spectra of (a) candle soot excitation peak at 259nm(b)carbon from HCL excitation peaks at 282 (c)Carbon from coconut shell major excitation peak at 740nm (near IR) (d)carbon using acid excitation peak at 245nm (e) Carbon from orange juice excitation peak at 284nm (f) comparison of all UV-VIS spectra

The Excitation of candle soot peak at 259nm which was similar to previously reported[26].The carbon prepared using sulphuric acid show peak at 245nm shown in (d) implies presence of sulphate ions and shows bathochromic shift from the previously reported work[28]. The Excitation peak at 284nm shown in (e) represents the presence of Rhodamine B[29,30] (fluorescent molecule) this shows the cnp-rod formation from orange juice. (c) doesn't have any excitation peak in UV-VIS region. (b) shows carbon prepared using HCL has absorption band at 282 similar to that of polycyclic aromatic hydrocarbons The red shift of the p–p* transition is dueto the extended conjugation in the structure of CNPs[31].



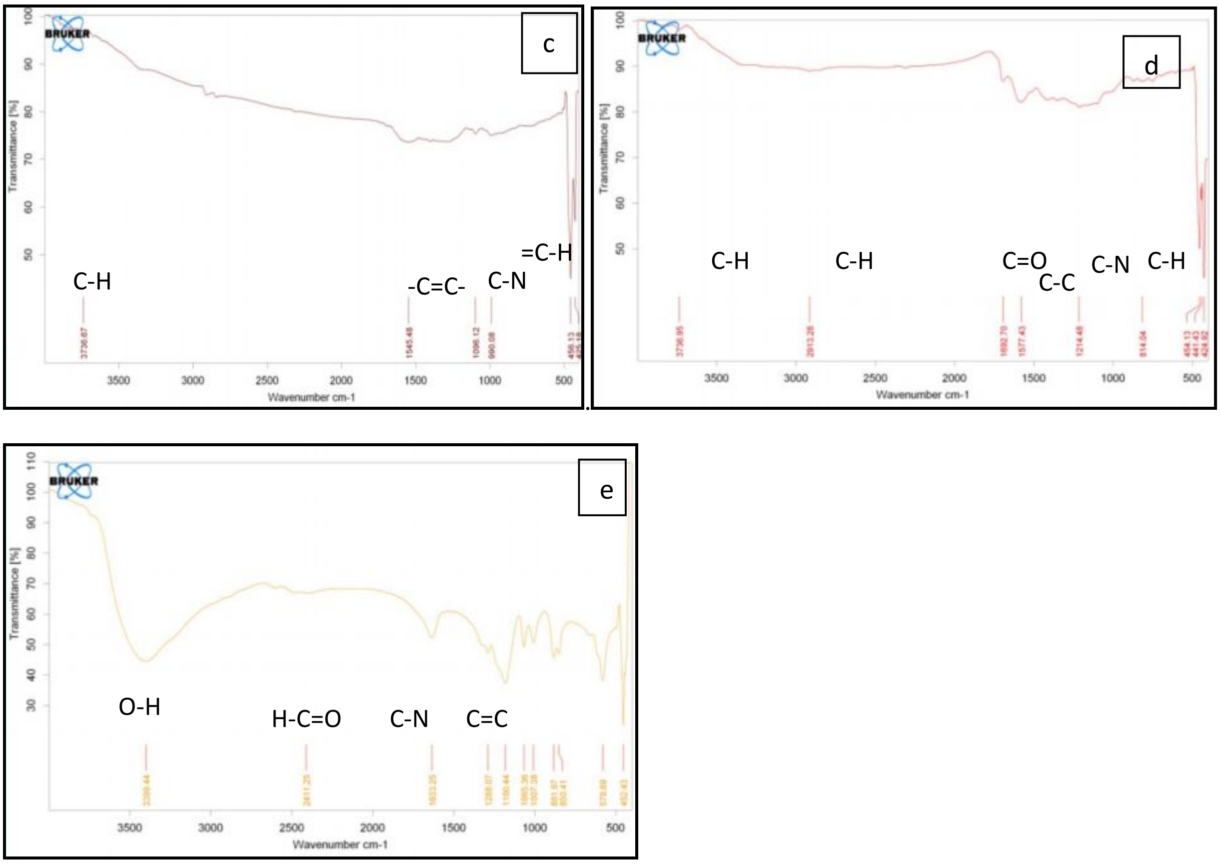


Figure 2 Represents FTIR spectra of (a) Carbon prepared from acid (b)Carbon prepared from coconut husk (c)Candle soot (d)Carbon prepared from coconut shell (e)Carbon prepared from sulphuric acid

The typical FTIR spectra of prepared carbon samples depict the organic compounds that might combined with carbon particles. Since charcoal absorbs hydrogen gas readily, so the C-H stretching in the Figure (b), (c) & (d) implies it has charcoal.-C-N- stretching depicts gas trapping ability of porous carbon structure.-C=C- stretching in Figure(a),(c)&(e) conform presence of aromatic compound in pairs which are residues of incomplete combustion.-C=O- implies the presence of hydroxyl group in Figure(a),(d)&(e) are oxidized residues.

SEM Analysis for Carbon from candle :

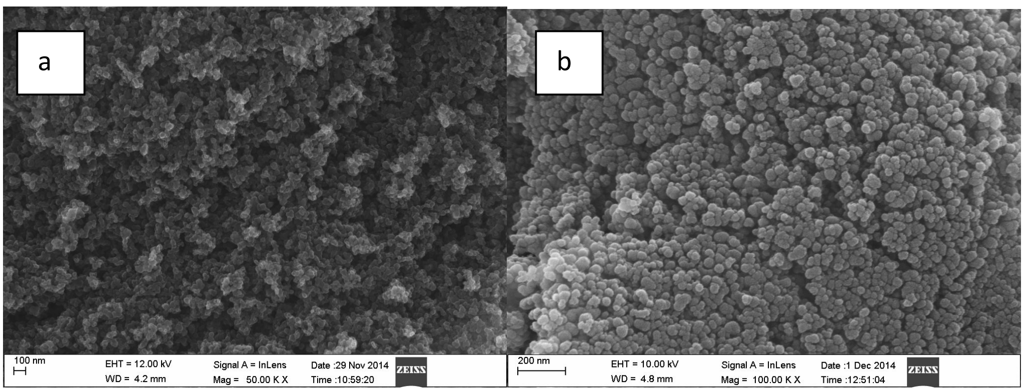


Figure 3: (a) shows agglomerated nanoparticles (form candle soot), (b) Shows Island like morphology of carbon clusters.

The incomplete combustion of wax produces elemental carbon shown by the equation

$C_{32}H_{64}O_2+O_2\rightarrow 25C+26H_2O$

Complete combustion of pentacosane (wax) produce carbon dioxide and water vapours but incomplete combustion producecarbon, carbondioxide, carbon monoxide and water vapour at different proportions.

These particles are made to deposited on the glass surface were investigated by Scanning Electron Microscope at different magnifications to characterize the surface morphology[25]. The particles nearly spherical in shape ranges between 40nm and 80nm in diameter [26]. These naturally prepared particles tends to agglomerate readily and eventually grow in island fashion, when these islands grows, form stack of monolayers. The similar kind of morphology also seen in charcoal residues. Therefore this reveals that naturally prepared particles agglomerates due to their vanderwaal's force of attraction. These particles are not soluble in polar solvents.

SEM Analysis for Carbon from coconut shell:

The naturally prepared carbon particles from residues of incompletely burnt coconut shell was crunched in motor and characterized using SEM shows different morphologies at different regions depicts irregular structures, spherical particles, and flakes[32].

The resultant particles approximately <1µm in diameter represented in (b)

The spherical particles show interconnected morphology and also a peculiar micro structure mentioned in (b)

The naturally prepared carbon particles tend to form various morphologies among that interconnected morphology of spherical particles is similar to that of figure 3.

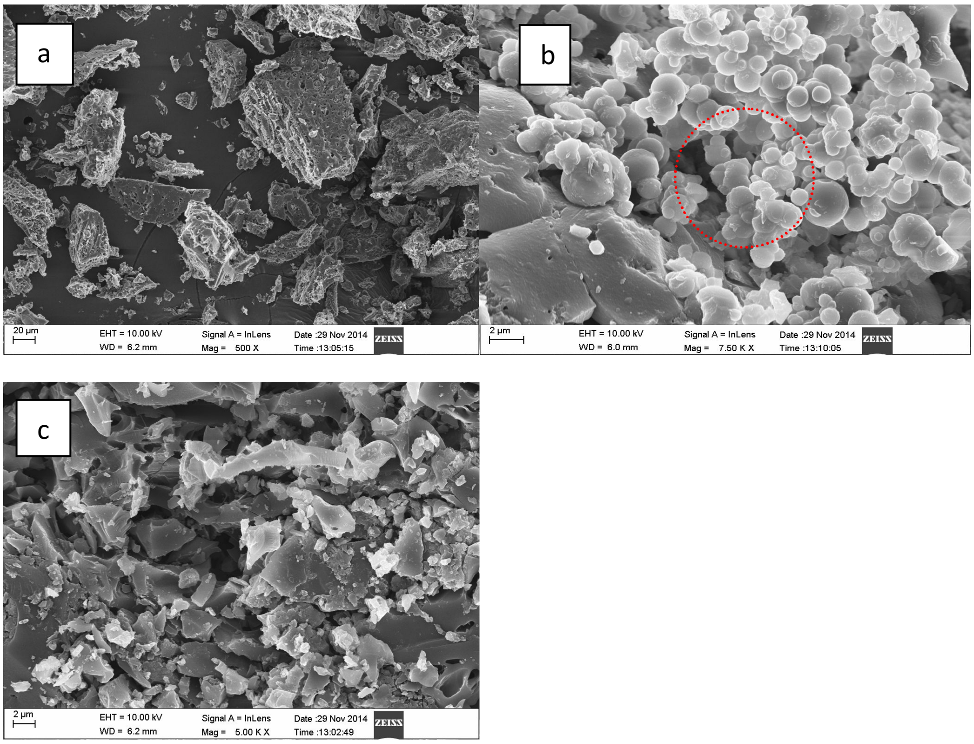


Figure 4: (a) shows the irregular micro structures of carbon from coconut shell (b) Represents the spherically shaped particles with interconnected morphology Dotted circle shows the peculiar micro structure ,(c) shows that the carbon particles forms non-uniform flake like structures.

SEM Analysis for Carbon from coconut husk:

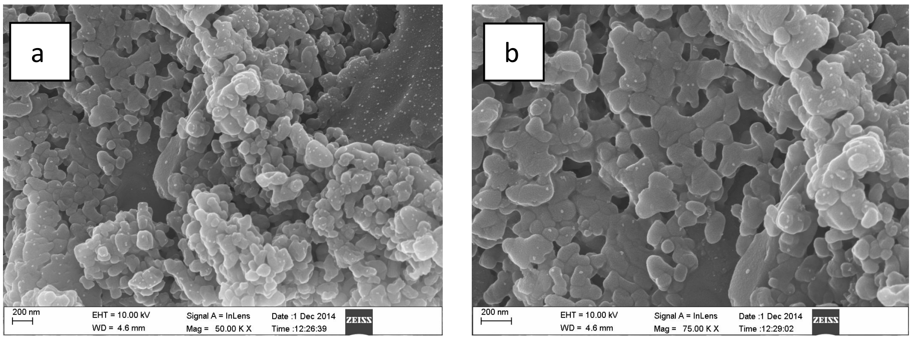


Figure 5:(a) shows the interparticle voids (b) shows the claver structure of carbon particles

The SEM characterization of residues prepared from incomplete combustion of coconut husk shows porous structure.Sphere accumulation/aggregation is a nice way to establish porosity.

Small spheres have quite a few advantages over the large ones to buildmesoporousinterparticle voids.

Sphere accumulation/aggregation is a nice way to establish porosity. Small spheres have quite a few advantages over the large ones to build interparticle voids.

SEM Analysis for Carbon particles using Acids:

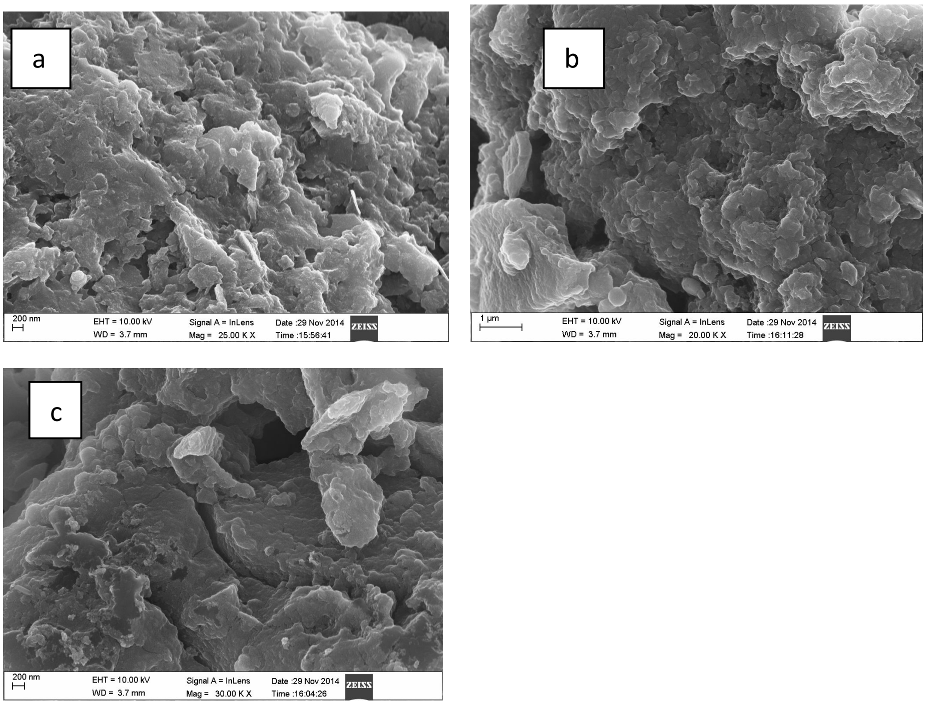


Figure 6: (a) shows the morphology of elemental carbon at nanoscale (b)and (c) shows variation in the morphologies at microscale.

When sugar mixed with con.sulphuric acid it produces SO_2 and lot of heat energy (exothermic reaction)
$C_{12}H_{22}O_{11}+H_2SO_4+1/2O_2 \rightarrow 11C+CO_2+12H_2O+SO_2$

In order to study actual morphology of resultant elemental carbon capping agents are not used. Therefore the particles aggregates into non-uniform structures.

The structure and morphologies of the particles are different at different length scales shown in figure 3(a),(b),and(c).

SEM Analysis for Carbon particles using Hydro chloric acid(HCL):

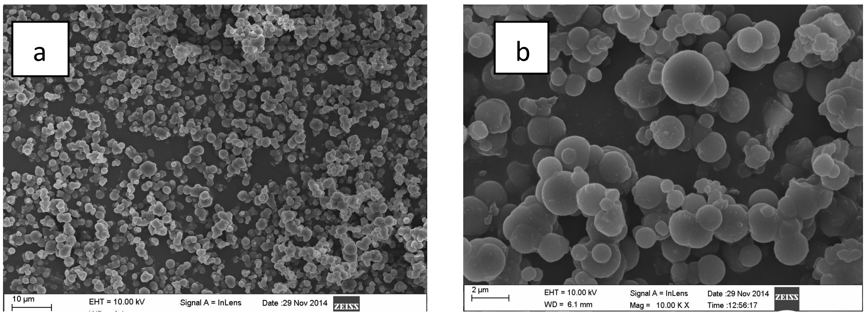


Figure 7: (a) and (b)shows the interconnected morphology of carbon particles investigated with different magnifications.

The hydrolysis of sugar produce glucose and fructose (each with con. 1 mol/L).
By adding hydrochloric acid(50ml) with the solution produces elemental carbon particles given by the equation
$C_{12}H_{22}O_{11}+HCl \rightarrow C+CCl_4+CO_2+H_2O$

Energy required to proceed this reaction is given by ultrasonication (sound energy).The resultant carbon particles are spherical in shape with diameter ranges between 1µm and 5 µm shows interconnected morphology[33] in (b).

Ultrasonic agitation enhances particle aggregation[34]. The aggregation of particles is less favorables in naturally prepared carbon particles in (a). This shows that the ultrasonic agitation increases the aggregation of particles in unique fashion rather than agglomeration of particles. The particles are connected strongly, not attached together by Vander Waals force.

Conclusion

Source	Morphology	Particle size
Coconut shell	non-uniform clusters ,flakes,spherical paricle	>1µm
Coconut husk	porous clusters	>1µm
Candle soot	Spherical particles(nanoscale)	40nm-80nm
Carbon particles using HCL	Spherical particles(microscale)	1µm-5um
Carbon particles using sulphuric acid	unusual non uniform structure	undertermine

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