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COMPARATIVE ASSESSMENT OF NANO-CARBON OBTAINED FROM VARIOUS BIOMASS PRECURSORS

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ABSTRACT

Carbon nanomaterials can be formed using agricultural and food waste. This has made it possible to use carbon nanomaterials for various applications. Their small scale is the reason of them having many interesting properties. These are used in the field of sensing, environmental remediation, bioimaging and energy related applications. Many types of these biomass are used in obtaining the nanocarbon materials such as fruit peels, coconut shells, rice husks, sugarcane bagasse, plant leaves and many more.

This review discusses the methods of synthesis, separation and various characterization techniques used to produce nanocarbon from biomass. This includes processes like hydrothermal treatment, microwave treatment, and pyrolysis. The type of biomass precursor will affect the properties of carbon dots or any other forms of nanocarbon, the properties also depend on the synthesis variable parameters and characterization techniques. The size of nanocarbon may vary, but typically are in nano-meter scale.

These obtained nanomaterials have many applications including fluorescent sensing, bioimaging, pollution detection, adsorption, photocatalysis and electrochemical storage. It is possible to produce useful nanocarbon materials from biomass waste which can prove aid in sustainable waste management. Also, it is very important to characterize these materials with standard process.

KEYWORDS - carbon quantum dots, hydrothermal carbonization, agricultural waste, fluorescence sensing.

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1. INTRODUCTION

Carbon nanomaterials have attracted much interest due to their optical, structural, surface chemistry and electronic properties. Carbon rich organic matter can be obtained from waste materials such as from fruit peels, leaves, coconut shells, rice husks, and sugarcane bagasse and by systematic approach processed to yield nanomaterials [1-3].

The properties of materials will change with type of biomass used in its synthesis to obtain carbon. Lignocellulosic biomass has variable amounts of cellulose, hemicellulose and lignin. Other biomass may contain high amounts of carbohydrates, protein and also inorganic matter.

When these components undergo carbonization, they chemically transform into carbon rich particles whose properties vary with the precursor [2,3].

the traditional biochar, porous carbon and carbon dots differ from one another, all of them are related but are not interchangeable. Biochar is a solid, rich in carbon material derived from biomass. Porous carbon has pores and specific surface properties. Carbon dots are nanoscale carbonaceous particles that are studied for their optical properties [2,3].

Carbon dots are getting recognition as their size and surface functional groups affect their optical properties, solubility and reactivity with chemicals [1, 2]. Here we are looking into various synthesis techniques, properties and the applications of the derived nanocarbons from various types of precursors.

2. METHODS OF SYNTHESIS

Carbon nanomaterials which are obtained from biomass are created by converting organic precursors. The type of biomass, reaction conditions and purification techniques will affect the properties of the final product [1, 3].

2.1 Pretreatment

the biomass pretreatment will ensure its readiness for carbonization. The biomass is collected, then washed with deionized/distilled water. After washing it thoroughly, it is dried and reduced in the size. The pretreatment is based on the type of biomass used. Rice husk contains inorganic silica which could affect the process and purity of the final carbon nanomaterial [2, 3].

2.2 Hydrothermal Carbonization

Hydrothermal carbonization is most studied method for the making of carbon dots from various biomass used as precursors. The biomass is heated in a sealed reactor where under high temperature and pressure the biomass undergoes several reactions including hydrolysis, dehydration, breakdown, condensation, nucleation and carbonization. This results in the formation of carbonaceous nanoparticles which surface functional groups [1,2].

The final particle size will depend upon the type of biomass precursor and variable conditions such as temperature, pressure, time, concentration and pH. The carbonaceous material can be purified by processes such as centrifugation, filtration and dialysis by separating large particles and soluble impurities [1, 2]. Abhinaya et al. treated coconut shell hydrothermally at

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250^0C for 6 hours to obtain carbon dots which were approximately of 2 nm in size.

2.3 Microwave assisted synthesis

Microwave assisted synthesis involves the use of microwave radiations to rapidly increase the temperature of precursors. This can cause carbonization depending upon the setup of reaction. Palm kernel shell and spent tea have been used as a precursor to make carbon dots using this process [2, 3]. The palm kernel was heated using microwave radiation of 385W for time of between 1 to 5 minutes producing carbon dots with high quantum yield which is 44%.[3]

2.4 Pyrolysis and thermochemical carbonization

Thermochemical carbonization is the process of heating the biomass under the absence or low O_2 environment. This process results in forming of volatile products and carbon rich solid. The type of material formed depends on the variable factors such as temperature, heating rate, residence time, surrounding atmosphere and composition of precursor. Depending on these conditions products such as bulk char, porous carbon or any carbon intermediates are expected [2, 3].

A carbon dot has been produced by using groundnut shells at 400^0C for 4 hours and a particle size between 0.4 to 2.4 nm with quantum yield of 10.58% was achieved [3]. These dots may not be formed directly by pyrolysis additional steps such as oxidation, separation and purification may be needed.

2.5 Nanoparticle production

Producing carbon nanoparticles is depended on the reactions that happen during carbonization and separation. Variable factors like temperature, reaction time, composition of precursor, concentration, pH, solvent and purification method should be optimized separately for each and every precursor to get the best out of it [1-3].

Carbon dots would not be obtained just by grinding it into a fine powder, they will be produced during the chemical or thermal decomposition and can be determined using characterization methods.

2.6 Purification and Characterization Techniques

The raw product may contain carbon particles of various sizes, unreacted compounds, soluble organic and inorganic matter. Centrifugation process can be used to remove larger particles and other aggregates. Filtration of the material is done so it separates material based on pore size. Dialysis can be used to remove small molecules. The purification methods affect the material`s composition and size of the product [1,2].

TABLE - IMPORTANT CHARACTERIZATION TECHNIQUES

TECHNIQUES	INFORMATION OBTAINED
Transmission Electron Microscopy (TEM)	Dimensions, morphology and size distribution of the particles
High-Resolution TEM (HR-TEM)	Fine structural features and possible fringes
X-ray Diffraction (XRD)	Structural order and diffraction features

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Raman Spectroscopy	Carbon structural disorder and graphitic domain information
Fourier Transform infrared spectroscopy (FTIR)	Surface functional groups
X-ray Photoelectron Spectroscopy (XPS)	Surface elemental composition and chemical states
UV-Visible Spectroscopy	Optical absorption characteristics
Fluorescence Spectroscopy	Excitation and emission behaviour
Dynamic Light Scattering (DLS)	Hydrodynamic particle-size distribution in suspension

3. PROPERTIES OF NANOCARBON DERIVED FROM VARIOUS BIOMASS

The properties of biomass-derived nanocarbons depended on precursor, the synthesis route and any post-treatment done. The values mentioned are from the specific studies in which they were measured and are not fixed properties for the biomass type.

3.1 Carbon Dots

Carbon dots and carbon quantum dots which are derived from biomass are zero-dimensional nanoparticles which are characterized by properties like photoluminescence, oxygen-rich surface functional groups and their ability to disperse in water[1, 2].They are synthesised by hydrothermal method by treating biomass at 180 to 250oC for 2 to 24 hours, though microwave-assisted, pyrolytic and low temperature methods have also been used[1, 4].The particle sizes reported ranging from 0.2 to 8 nm, to be precise 1-4 nm for cassava pulp [1], 6 nm for bamboo leaves[1], 0.2-2.2 nm for potato peel [1], 0.4-2.4 nm for groundnut shell [3], and roughly 2 nm for coconut shell [6]; particles of approx. 25 to 30 nm have been reported for rice husk [4, 5, 9]. Fluorescence quantum yield differ from around 2% for dead neem leaves[2], 4.7-14.81% for sugarcane bagasse and avocado peel[1], 20% for wheat straw[3], 36% for orange peel[2], 44% for palm kernel shell [3], 48% for banana pseudo stem [2], and 53.46% for corncob [4].rice husk derived dots have been reported to have quantum yields ranging from 3% to 66.4% across various studies[4, 5].Coconut shell derived carbon dots are stable, negatively charged, spherical shaped and amorphous in nature [6], while rice husk derived dots in one study showed excitation-dependent emission, 98% cell viability and anti-inflammatory activity [9].

3.2 Graphene-like sheets, graphene oxide and reduced graphene oxide

Graphene-like sheets have been made from biomass and carbohydrate feedstocks through H_2SO_4 dehydration-condensation at room temperature [10], and also from recycled fibreboard by catalytic graphitization [11]. These materials have porous graphitic nanosheets which may enhance electrolyte access and ion transport.

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This reflects graphitic ordering instead of perfect graphene crystallinity [11].

Graphene oxide retains the oxygen-rich functional groups that control surface reactions and their dispersibility in liquids. It has obtained from various precursors such as rice husk, sunflower stalks, corn cobs, spent coffee grounds, spent tea leaves, coffee waste and food waste biochar, using method of low-temperature combustion with ferrocene catalyst or by pyrolysis which is then followed by modified hummers methods [12-15].

3.3 Carbon nanotubes and carbon nanofibers

Carbon nanotubes are 1-dimensional structures whose properties such as electronic, mechanical and surface chemistry depends on factors like number of walls, diameter of nanotubes, graphitic ordering and presence of defects [16]. Carbon nanofibers are filamentous carbon materials which are made by process such as electrospinning, stabilization and carbonization or catalytic growth methods [17].

3.4 Porous, heteroatom doped and nanosheet carbons

Porous carbon can be synthesized from biomass precursors such as coconut shell, rice husk, groundnut shell, wood, lignin using carbonization followed by either chemical or physical activation. This provides various properties depending on source, activating agent and pore structure [18, 19]. Peanut shell-derived carbons showed amorphous and disordered structure with micro, meso and macro pores. Activation of these carbons using various activating agents improved their surface area. The surface area was 1457 m^2/g with $KHCO_3$, 1625 m^2/g with K_2CO_3 and 2547 m^2/g using KOH [7]. A large surface area does not always promise high capacitance due to the differences in the pore accessibility, conductivity and surface chemistry.

By doping these materials with heteroatoms can change their surface chemistry. N/O/S doped hierarchical porous carbons from kraft lignin using direct pyrolysis method without any activating agents or templates showed surface area ranging between 338 and 1307 m^2/g and high heteroatom content (9.84 - 19.91 wt%) [19].

Cedar cone derived nitrogen doped porous carbon nanosheets which were activated using KOH at 700^oC showed surface area of 2238 m^2/g, high pore volume of 1.26 cm^3/g, high conductivity off 11.03 S/cm, capacitance of 290 F/g, cycle stability with 93.4% retention after 1000 cycles, energy density of 40.27 Wh/kg and power density of 208.19 W/kg [20].

4. APPLICATIONS OF NANOCARBON FROM DIFFERENT BIOMASS SOURCES

4.1 Sensing and bioimaging

As the fluorescence of biomass derived carbon dots responds to the chemical environment it is applied in optical sensors and imaging probes [1-4]. Wheat-straw derived dots have been studied for the detections of Fe^3+ and the groundnut derived dots for Cu^2+ [3], the palm kernel dots are studied for metal-ion sensing and imaging applications [3], corncob dots for biomolecules and metal-ion sensing [4], and lettuce leaf derived dots for detection of antibiotic metronidazole [4]. Rice husk dots

are have being studied for sensing, bioimaging and environmental detection [4, 5]. Bioimaging application of avocado peels and sugarcane bagasse is proposed [1], banana pseudo stem [2], mango kernel dots [4] and orange peel dots have been studied for photocatalytic uses [2]. In electrochemical sensing, food waste biochar derived GO on a screen-printed carbon electrode has been provided selective dopamine detection as its negative surface attracts dopamine while repelling uric and ascorbic acid [15].

4.2 Energy storage

carbon materials resembling graphene have been investigated for the applications in supercapacitors and Li-ion batteries which are made from recycled fibreboard and biomass or carbohydrates [10, 11]. Most developed carbon materials ae porous in nature. Peanut shell derived carbon has been studied for usage in high energy ultra-capacitor electrode materials [7]. coconut shell, rice husk, wood and lignin-based carbons are studied for their utilization into supercapacitors and batteries [18, 19]. Kraft-lignin based N/O/S doped carbon has been synthesized for high-performance supercapacitors [19]. Cedar cone nanosheets have demonstrated a high capacitance of 290 F/g at 1 A/g with capacitance retention of 93.4% for over 1000 cycles [20].

4.3 Environmental remediation and composites

GO derived from precursors such as rice husk, sunflower stalks, corncobs, spent coffee grounds, spent tea leaves and coffee waste has been proposed for applications like adsorption, sensors, and composites, with oxygen containing surface groups which interact with contaminants and host materials [12-15]. Bagasse derived rGO is a promising variety for conductive composites and environmental materials [10,13]. Porous carbon material derived from agricultural residue are also studied for purposes of adsorption, water treatment and catalysis [18, 19].

4.4 Catalysis and other proposed uses

CNTs and CNFs are generally studied for the applications such as conductive composites, catalysis, sensors, filtration and electrodes [16, 17]; nanoflakes for electrodes, catalysis and sensing [21]; carbon aerogels studied for energy storage, adsorption, thermal insulation, sensing and catalysis [22]; and ordered mesoporous carbon for supercapacitors, batteries, catalysis, separation and adsorption purposes [23].

5.CONCLUSION

There is a great potential for the use of biomass derived nanocarbon materials to utilize waste from agriculture and food production. It can be seen that there are many precursors which can be used to produce variety of nano-carbons.

The methods used to synthesis these kinds of material are the key which includes hydrothermal carbonization, microwave assisted synthesis and pyrolysis. The material produced will depend upon the composition of precursor, the reaction conditions, carbonization and purification methods. The size of particle needs to be confirmed to be in a nano-meter scale by appropriate characterization techniques [1-3, 6].

There are variable results for the particle size and fluorescence quantum yields throughout the literature studied. The fluorescence

quantum yield and pure dry mass yield should be appropriately differentiated.

The material can be useful in variety of areas like fluorescence sensing, bioimaging studies, environmental sensing for pollutants in surrounding, adsorption, photocatalysis and energy related applications. Carbon dots are a reliable option for optical sensing but due to is porous nature it is usually the better option for traditional electrodes for supercapacitors [1, 4, 7, 8].

There are still some issues related to these materials. The variability of precursors, yields are not always fully reported, inconsistent particle size and further purification is also required. In future, the work should be focused on consistent synthesis methods, particle size distribution, quantification of the mass yields and assessment of the performance of the material where it performs the best.

Overall biomass derived nanocarbon is a promising area to look into with combining it with waste valorization and nanotechnology. To make this useful in real time, the materials need to have consistent properties and their performance to show potential.

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