

Review Paper:

Synthesis of Value Added Nanoparticles from Biomass Resources

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prasadbobinda06@gmail.com**Abstract**

The utilization of sustainable biomass materials provides a versatile route for the development of new alternatives to replace traditional petro-materials for a variety of purposes such as green energy, paint, food packaging and biomedical applications. This study reviews the potential use of various sustainable biomass materials for the production of low-cost, high-value-added materials for practical applications including bio-printing, drug delivery/controlled release, tissue engineering, energy storage and bio-sensing.

This study highlights the fabrication of novel nanomaterials from various biowastes including crop residue, food waste and industrial waste (e.g. spent battery waste and polythene waste) through physical, chemical, or biological methods.

Keywords: Biomass, Carbonaceous materials, Activated carbon, Carbon dots, Metal oxides.

Introduction

Nanoparticles (NPs) and nanostructured materials (NSMs) have gained more attention in globalization as well as industrial application due to their exceptional physio-chemical properties such as melting point, wettability, electrical and thermal conductivity, catalytic activity, characteristic absorption or emission and scattering of light resulting and varying from their bulk counterpart and their chemistry. Nanomaterials have the potential to improve the environment via direct or indirect applications to detect, control, prevent and remove pollutants, as well as indirectly employing well-developed nanotechnology to design or distinguish cleaner industrial processes and create environmentally responsible products.⁴⁹

By definition, materials that have at least one dimension with length in the range of 1–100 nm are described as nanomaterials. A nanometer (10^{-9} m) is one hundred thousand times smaller than the diameter of a human hair, a thousand times smaller than a red blood cell, or about half the size of the diameter of DNA.⁴⁹ There are several definitions of nanomaterials suggested by different organizations, however, a single internationally accepted definition of nanomaterials does not exist yet. It is well known that the phases, sizes and morphologies of nanomaterials have a great influence on their properties and

potential applications; thereby, the controlled synthesis of nanostructured materials with novel morphologies has recently received much attention.

Nanomaterials have been attracting great attention in almost all engineering sectors and are widely distributed over all kinds of products that are used for basic human needs such as medicine, engineering, environment, electronics etc. In upcoming days, the nanotechnology controls mankind in living, working and communicating fields.

Nanomaterials may be of different shapes and structures at the nanoscale level. These can be classified and characterized based on their dimensionalities like 0D, 1D, 2D and 3D. In zero-dimensional, all the three dimensions of the materials are in the nanoscale range (nanoparticles, quantum dots). In one dimension any one dimension will be in the nanoscale range (Nanorods, nanotubes, nanowires). In two-dimensional, any two dimensions are in the nanoscale range (Nanofilms, nanolayers.) whereas three-dimensional nanomaterials are not in the nanoscale range and are generally referred to as bulk nanomaterials which include nanocomposites, core shells, multi nanolayers, bundles of nanowires etc.

Nanomaterials can be further classified according to their appearance, morphology, size, properties and the constituents in it. They are carbon based nanomaterials, inorganic or organic based nanomaterials, semiconductor nanomaterials and composite based nanomaterials as shown in table 1.

Apart from that NPs and NSMs can also be classified based on their origin. Some nanomaterials are produced incidentally as a by-product of different industrial processes and combustion processes such as vehicle engine exhaust as well as some natural processes such as forest fires, photochemical reactions, volcanic eruptions etc.

Moreover, the synthetic or engineered nanomaterials are those which have been manufactured by humans through the physical, chemical, biological or hybrid process to achieve the required properties for desired applications.²² In recent times, several feedstock were used in the production of various materials to drive toward sustainable development. It is well known that biomass is an effective source of renewable energy; it contains stored chemical energy from the sun and can be burnt directly for heat or conversion into renewable liquid and gaseous fuels through various processes.

Table 1
Different types of nanomaterials and their characteristics

Nanomaterials based on constituent	Characteristics	Examples
Carbon based nanomaterials	Carbon is the main constituent. Shows good electrical conductivity, electron affinity and high strength	Fullerenes (C ₆₀), carbon nanotubes (CNTs), carbon nanofibers, carbon black, graphene etc.
Inorganic or organic based nanomaterials	Contains metal and metal oxide or organic matters. By doping different elements in different constitutions novel properties can be achieved. Widely used in environmental and bioimaging studies.	Au or Ag NPs, TiO ₂ , ZnO etc.
Semiconductor nanomaterials	Contains metallic and non-metallic properties, widely used in photocatalysis and electronic devices.	ZnS, ZnO, CdS, GaN, GaP InS etc.
Composite based nanomaterials	A polyphase solid material where one of the phases has one, two, or three dimensions in the nanoscale range. It may be any combination of carbon-based, metal-based, or organic-based NMs.	Graphene-based composites, Metal oxide/AC composites etc.

Some estimates predict that biomass will account for 15% of the world's total energy supply and 38% of the primary energy consumption in developing countries. Biomass resources can be the potential raw materials to produce different materials having unique characteristics and attract more attention for materials production.

More recently, hydrothermal treatment of crude biomass has been used for the production of several carbonaceous materials including nanotubes, nanofibers, monodispersed microspheres and porous materials.

Pyrolytic decomposition of crude biomass yields surprising nanostructure materials which can be used for desired applications. Moreover, crude biomass as feedstock offers several advantages in terms of cost and environmental issues and towards waste management with reasonable utilization. With the increasing explosive growth of industrial applications, transportation has brought about several environmental problems as well and generates a huge amount of waste as by-products.

There is an urgent need to follow all the fundamental principles of 'green' chemistry to develop and synthesize simple, eco-friendly and cost-effective approaches for the preparation of advanced materials for basic human needs.

Therefore, researchers show more interest in the waste minimization and implementation of sustainable processes by reutilization of primary wastes into value-added materials.⁵⁸ Numerous biomass resources such as wood and wood processing wastes, agricultural crops and waste materials, municipal solid wastes, dead leaves and forestry wastes have been utilized as a valuable feedstock for the synthesis of various nanostructured materials which can be used in the desired application.

Nanoparticles from biomass

In the energy generation, biomass has a significant role to be an eco-friendly fuel converted by a different process such as combustion, gasification, pyrolysis, incineration etc. Combustion of biomass yields 70 kg ash per ton on average and the burnt ash consists of crystalline and amorphous materials having a high specific surface area which may adsorb toxic harmful materials and damage to human health.²⁹ Development of carbon-based nanoparticles from biomass-derived carbon precursor materials is seeking more attention due to their easy availability, economic viability, cost efficiency and easy synthetic route.⁵⁵

Besides that, different forms of carbon-based nanomaterials such as graphene, fullerene, carbon nanotube, activated carbon NPs etc.⁵³ have distinct physical and chemical properties, surface morphology, uniform particle size, biocompatibility and large surface area. Utilization of various biomass-based carbon nanoparticles from different carbon source materials like coconut shell, cooking oil, rice bran and wood etc. had been reported.^{16,20,48,63}

Reutilization of biomass power plant fly ash can produce silica material in amorphous and mesoporous nano-scale range to reduce the hazard of ash landfill for the environment.³ The preparation of nano-sized gold materials has become very important due to its unique properties and their potential utilization in new developing technologies such as catalysis, chemical industry, biotechnology, electronics and electro-optical devices.

Several techniques have been reported to prepare gold nanoparticles such as ultraviolet irradiation, aerosol technologies, lithography, laser ablation, ultrasonic fields and photochemical reduction of Au.

However, to reduce the production cost and the use of hazardous materials, researchers made intensive efforts in the development of cost-effective and eco-friendly methods to reduce Au (III) and form Au nanoparticles. In a study, oat (*Avena sativa*) biomass was utilized as an alternative to recover Au (III) ions from aqueous solutions and studied its capacity to reduce Au(III) to Au(0). Oat biomass formed Au nanoparticles of FCC tetrahedral, decahedral, hexagonal, icosahedral multitwinned, irregular and rod shape by reacting with Au(III) ions.²

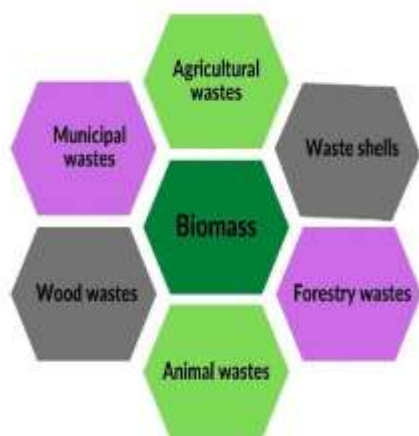


Figure 1: Different types of biomass resources

In another study, dried biomass of *parkia roxburghii* leaf was used for the synthesis of gold (Au) and silver (Ag) nanoparticles (NPs) through a green synthesis approach. The leaf biomass acts as both reductant as well as stabilizer and studies revealed the formation of face-centered cubic structure NPs with average crystallite size of 8.4 and 14.74 nm for both Au and Ag respectively. The resultant TEM image showed the Au NPs as monodispersed with spherical shape in the range of 5-25 nm whereas Ag NPs appeared as a polydispersed and quasi-spherical shape in the range of 5-25 nm.³⁷ Biological syntheses of gold nanoparticles using biomass of *Aspergillus fumigatus* were also reported.

Aspergillus fumigates biomass acts as a reducing agent in an aqueous solution of chloroauric acid (HAuCl_4). The biosynthesized gold nanoparticles in the size of 85.1–210 nm were confirmed by EDS analysis.⁴ The silver (Ag) nanoparticles prepared from dried Piper betle biomass leaves through a facile, one-pot and environmentally benign method exhibited unique spherical configuration and face-centered- cubic structure with preferred (1 1 1) orientation.³⁹ Rice husk (RH) biomass is a potential source of renewable energy obtained from rice milling as a by-product. The major components of RHs are mainly lignocellulose (72–85 wt %) and silica (15–28 wt %).⁶

Silica or other silicon-based materials can be recovered from rice husk with high purity and high surface area which are important elements in manufacturing high value-added products and ensure efficient utilization of a bioresource. The average size of the produced silica particles was

approximately 60 nm.^{8,60} However, the structures of silica particles obtained from RHs appear to be much simple and less visually attractive as compared to the diatoms, although the large quantities of RH biomass offer an opportunity for mass production of nanostructured silica for various applications.⁵⁴

In a study, photoluminescent carbon quantum dot grafted silica nanoparticles (silica-C NPS) were directly synthesized by using rice husk biomass and the derived NPs exhibit excellent surface modification, high water dispersibility as well as biocompatibility.⁵⁸ In an experiment, bamboo (leaf biomass) was used as a precursor for low-cost indigenous production of silica nanoparticles through thermal combustion and alkaline extraction and their physicochemical properties were investigated. The experimental results revealed that primed silica powder exhibits amorphous particles (average size: 25 nm) in a spherical shape with a high specific surface area ($428 \text{ m}^2 \text{ g}^{-1}$).⁴⁰ In another study, spherical mesoporous activated carbon (SM-AC) nanoparticles were synthesized from green tea wastes using KOH activation for anode material of lithium-ion battery (LIB).

The obtained nanoparticle showed a high surface area ($1241 \text{ m}^2 \text{ g}^{-1}$) and high porosity in nature so that it can appear as a superior candidate for anode material of high-performance LIBs.⁴⁴ De-oiled biomass or oilseed cake can be further utilized in the biosynthesis of metal nanoparticles. Biosynthesized polydispersed, spherical shaped silver nanoparticles with 2-20 nm size were reported from de-oiled biomass of thermotolerant oleaginous microalgae *acutodesmus dimorphus*.⁷

Synthesis of various metal oxide nanoparticles from biomass resource by several methods such as the ultrasonic-assisted method, the hydrogen plasma-metal reaction method, microwave-assisted method, facial calcinations, direct thermal decomposition, chemical co-precipitation, two-step process (green synthesis) and two-step thermal decomposition was also reported.^{49,31} Waste eggshell can be considered as a potential candidate for the synthesis of calcium oxide nanoparticles. Utilization of waste eggshells as a precursor for the synthesis of CaO nanoparticles makes the whole process greener and the nanoparticles produced through the sol-gel technique were almost spherical in morphology within the range of 50 nm–198 nm.¹⁴

Nanoparticles derived from Shrimp shells exhibit effective antimicrobial activity against gram-positive and gram-negative bacteria. Shrimp shells act as a green source of precursors synthesized calcium oxide nano-plates ranging from 40 to 130 nm (in length) and 30 to 100 nm (in width).¹¹ Moreover, the formation of metal hydroxide nanoparticles from biomass resources was also reported.^{24,36} In a study, chicken eggshells were used as a precursor for the development of bio-material calcium hydroxide nanoparticles (Ca(OH)_2).³⁶ Formation of Nickel oxide

nanoparticles by dead biomass of filamentous fungus was reported.⁴¹

Synthesis of nanoparticles

Bio-wastes or biomass can be transformed into various value-added nanomaterials either physically, chemically, or biologically. However, the highly heterogeneous nature of biomass creates a challenging task to identify methods for their valorization and transformation.²¹ The physical methods are further categorized as "top-down" and "bottom-up" approaches whereas in the "top-down" approach, the larger materials are squashed into smaller particles by mechanical milling, thermal and laser ablation technique.⁴⁵ These are easy to perform but not suitable for preparing informal shaped and very small size particles as it changes in surface chemistry and physicochemical properties of nanoparticles.

In the bottom-up method, smaller nanostructured particles act as building blocks to produce final nanoparticles. The chemical synthetic route shows a variety way of bottom-up synthesis techniques for the preparation of nanoparticles such as sol-gel method, co-precipitation, hydrothermal technique, solvothermal, sonochemical, pyrolysis, vapor deposition, microemulsion, microwave-assisted, intercalation, ion-exchange etc.^{15,18,25}

In a study, novel and efficient silica-based photo luminescent nanostructures were developed from RH biomass using the ultrasonication method for biomedical applications.⁵⁸ A study reported a sustainable biogenic synthesis of silver nanoparticles using lipid extracted residual biomass of microalgae *acutodesmus dimorphus* cultivated in dairy wastewater.⁷

Besides, being simple and economic, the sol-gel technique has many advantages over the other mechanism for synthesizing metal oxide nanoparticles as it requires low temperature and pressure. The utilization of waste materials as a novel and green source of precursor for value addition makes the whole process cheaper, green and sustainable. Synthesized calcium oxide nanoparticles from eggshell through the sol-gel method exhibit unique physiochemical properties and can be considered as a promising resource of calcium for the application of versatile fields.¹⁴

In another study, a green synthesis of CaO NPs from shrimp shells was investigated using a two-step process. At first, the dried shrimp shell powder was treated with diluted hydrochloric acid to obtain CaCl_2 which was further converted to CaCO_3 by treating it with a Na_2CO_3 solution.

In the second step, the resulting CaCO_3 was subjected to calcination to deliver the desired nano-plate size CaO.¹¹ Synthesis of calcium hydroxide nano-plates (GCHNPs) was first reported from waste oyster shells using a chemical precipitation method in an aqueous medium at 90 °C without using any additives. The obtained nanostructure exhibits a crystal size of around 350–450 nm and a specific surface area of $4.96 \text{ m}^2\text{g}^{-1}$ confirmed by field emission scanning electron microscopy (FE-SEM) and Brunauer-Emmett-Teller (BET) respectively.²⁴

Moreover, catalyst-free carbon nanospheres were synthesized using simple one-step pyrolysis techniques where biowaste sago bark is used as a carbon precursor and obtained carbon nanospheres showed porous nature and revealed that more than 95% carbon is present in the synthesized carbon nanospheres with particle size ranging from 40-70 nm.¹⁶

Table 2
Different types of nanomaterials from biomass resources

Biomass precursor	Prepared nanomaterials
Parkia roxburghii leaf	Gold and silver nanoparticles ³⁷
Rice husks	Silica nanoparticles ⁸
Bamboo leaf	Silica nanoparticles ⁴⁰
Tea wastes	Activated-carbon nanoparticles ⁴⁴
Waste eggshell	Calcium Oxide nanoparticles ¹⁴
Waste eggshell	Metal hydroxide nanoparticles ³⁶
Shrimp shells	Calcium Oxide nanoparticles ¹¹
Waste oyster shells	Calcium hydroxide nanoparticles ²⁴
Sago bark	Carbon nanospheres ¹⁶
Sugarcane waste	Nanoporous activated carbon ²⁰
Wood wool	Carbon nano-onions ⁴⁸
Cassava's peels	Carbon dots ³⁸
Rapeseed oilcake	Carbon nanoparticles ⁹
Banana fruit waste	Gold nanoparticles ¹⁰
Waste chicken eggshell	N-doped fluorescent carbon nanodots ²³
Waste coffee grounds	Porous carbon nanosheets ⁶²

Further, a study demonstrates the synthesis of fluorescent C-dots from cassava's peels using low-temperature green synthesis base. The whole synthesis techniques were done by using water as a solvent non-chemical and natural source in an environment-friendly manner.³⁸ Hydrothermal carbonization is an effective technique for the conversion of industrial waste into value-added carbon nanoparticles. The results acquired show the ability to convert industrial biowaste into useful nanomaterials for use in food industries and also indicate new scalable and simple approaches to improve environmental sustainability in industrial processes.⁹

Applications of biomass-based nanostructures

The application of nanoparticles is almost widely found in every sector due to its unique and tunable magnetic, electrical, optical and chemical properties. Nanoparticles are used as sensors, biosensors, biocatalysts in the area of biomedical, waste management and modern information technologies.^{3,17,27,32,43,46,50} Besides that, they are applicable

in the form of electrodes for batteries and supercapacitors as well as different energy storage devices. Nanoparticles are widely used in medical sciences due to their unique optical and chemical properties. Biomass-derived carbon dots exhibit superior properties such as water solubility, low toxicity, biocompatibility, small size as well as fluorescence and photoluminescence for desired practical application. Its specific optical properties like tunable photoluminescence and up-photoluminescence have led to remarkable use in medical sciences including bioimaging, sensing and drug delivery.^{31,56}

Synthesis of fluorescent carbon dots from biomass resources offers green techniques for selective and sensitive detection of the toxic metal ion.^{19,33,53} Biomass-based nanoparticles show excellent absorbent properties which can be further applied for the removal of heavy metal ions.³⁴ The nanoporous activated carbons obtained from biowastes exhibit superior catalytic activity and also possess high specific surface area with well-decorated pore size.

Table 3
Different types of techniques for nanomaterial synthesis

Methods		Advantages	Disadvantages
Biological methods	By using microorganisms like bacteria, fungi, algae	Eco-friendly, simple and easy, a single step is required.	Safety measures are required due to the pathogenic nature of microorganisms.
Physical methods	Laser evaporation method	Easy, fast and straightforward method. It does not require long reaction times, high temperatures, or multi-step chemical synthesis.	Possibility for the formation of "colloidal alloys," that consists of alloy NPs or a mixture of different types of materials.
	Mechanical milling	Large scale production of high purity nanoparticles with superior physical properties.	Required high energy and an extensively long period of milling time.
	RF plasma method	Narrow size distribution and continuous synthesis with controlled surface morphology.	Chances of chemical hazards because of toxic, corrosive and explosive precursor gases.
Chemical methods	Co-precipitation method	The uniform pure and controlled nanoparticles size can be obtained.	Requires the aqueous medium for precipitation. Solvent separation and further purification are needed.
	Sol-gel method	Suitable for gas or liquid phases, simple procedure.	Purity is less due to the formation of composites in it. Post-treatment is required for the purification of the sample.
	Hydrothermal method	Good quality crystals with controlled composition, Highly homogeneous nanoparticles can be achieved	Processes are difficult to control, limitation of reliability and reproducibility.
	ultrasonic irradiation method	Green, safe, fast and easy method. Suitable for less volatile organic liquids.	The rate of reaction completely depends on the ultrasonic frequency
	Microwave-assisted method	Shorter reaction time, narrow size distributed small size particles can be prepared.	The rate of reaction completely depends on microwave radiation.

Besides that, the biomass-derived nanostructures offer high specific capacitance at low cost in a green sustainable pathway and that is why they can be considered as suitable electrode materials for supercapacitors.^{52,55} Silica-based luminescent materials derived from rice husk biomass contain two forms of carbon and show a luminescent mechanism which would be valuable for researchers to further modify the luminescent features for practical applications.⁵⁶

The uniformly-distributed spherical nanoparticles SiO_2 from rich husk also have been exploited for the application of energy storage and drug delivery. Crystalline and uniform particle size distribution highly pure silica is a valuable starting material for the fabrication of battery materials. Synthesis of silica nanoparticles from bamboo (leaf biomass) through thermal combustion and alkaline extraction exhibits amorphous particles (25 nm in size) with high surface area ($428 \text{ m}^2 \text{ g}^{-1}$) and spherical morphology. The synthesized silica nanoparticles show extensive capability in the biomedical field which can be used in drug delivery via cost effective route.⁴⁰

Conclusion

Nanomaterials derived from biomass resources such as the raw materials from agricultural processes, ocean plants and

animal residues, have emerged attention to develop new materials. Using the products from sustainable biomass materials contributes considerably to the economic viability and provides a green economic route. Therefore, sustainable-material derived from biomass residues has been broadly applied in energy storage, packaging, sensing, catalysis and even biomedicine.



Figure 2: Applications of nanomaterials in different fields

Table 4
Different types of nanomaterials from biomass and their applications

Biomass source	Prepared nanomaterials	Application
Wheat flour	N- doped porous carbon	Reduction of CO_2 to CO ²⁸
Sodium alginate	Carbon nanoparticles/graphene Composites	Lithium-ion batteries ⁶⁰
Beetroot	Activated carbon supported Fe_3O_4	Reduction of nitroarenes ⁵¹
Cornstalk	Graphitic carbon nanosheets	Supercapacitor electrode ⁵²
Cellulose	Porous N- doped carbon	Supercapacitor electrode ⁵⁵
Waste cotton	Magnetic porous carbon	Microwave absorption ⁵⁹
Chitosan	N-doped carbon	Electrocatalysis ⁶⁴
Jackfruit peel	$\text{Ni}(\text{OH})_2/\text{AC}$ composites	Microwave absorption ¹²
Tea wastes	Activated carbon nanoparticles	Lithium-ion battery ⁴⁴
Shrimp shells	Calcium oxide nano-plates	Antimicrobial activity against gram-positive and gram-negative bacteria ¹¹
Sugarcane waste	Nanoporous activated carbon	Supercapacitor electrode ²⁰
Cassava's peels	Carbon dots	Bioimaging and biosensing ³⁸
Waste chicken eggshell	Nitrogen-doped fluorescent carbon	Stamping, printing and forensic applications ²³
Black tea	Carbon dots	Detection of Fe^{3+} ²³
Plant leaf	Carbon dots	Sensing, patterning and coding ⁶⁵
Rice husk	Carbon dots	Bio-imaging ⁵⁷
Piper betle	Silver nanoparticles	Nitrite detection ³⁹
Bamboo leaf	Silica nanoparticles	Drug delivery ⁴⁰
Corn cob	AC-ZnO composite	Adsorption of cations ⁸
Peanut shells	$\text{MgO}/\text{Fe}_3\text{O}_4$ nanoparticles	Adsorption of malachite green ¹³

Moreover, their physical and chemical properties including specific capacity (for energy storage application), the surface area for catalytic or adsorptive activity are often found to be greatly effective towards practical applications. Biomass-derived porous carbon materials have been investigated in fuel-cell research and development extensively due to their outstanding properties such as electrical conductivity, stability, tunable morphology and functionality. In this review, we provided insights into the production of nanostructures from various wastes (biological and industrial wastes) and major techniques employed for synthesis and their application in the various sector were succinctly summarized. Reutilization of biomass materials for the value addition of nanostructures demonstrates a vital path in the field of waste and environment treatment as well as their new-age applications from biomedical to energy storage, which was explored for enhancing the circular economy.

However, although biomass resources provide an endless source to synthesize different materials, several ongoing limitations are also there. The purity and sources of biomass materials and the solubility of some biomass-based materials are concerns for their use in biomedical applications. Therefore, some biomass materials require further modification or blending to enhance their physicochemical properties for desired applications.

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(Received 10th March 2021, accepted 10th May 2021)
