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Akrity Singh Bharadwaj
Department of Chemistry, Ewing Christian College, University of Allahabad, Uttar Pradesh, India

Gautam Kumar
Department of Chemistry, Ewing Christian College, University of Allahabad, Uttar Pradesh, India

Justin Masih
Department of Chemistry, Ewing Christian College, University of Allahabad, Uttar Pradesh, India

Correspondence
Akrity Singh Bharadwaj
Department of Chemistry, Ewing Christian College, University of Allahabad, Uttar Pradesh, India

Green synthesis of carbon nanotubes from agricultural wastes: A review on pathways, challenges, and future prospects

Akrity Singh Bharadwaj, Gautam Kumar and Justin Masih

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Abstract
Carbon nanotubes (CNTs) are among the most important nanomaterials that have been found in the last thirty years because of their exceptional mechanical strength, high aspect ratio, thermal stability, and special electrical characteristics. Although hydrocarbon gases, petroleum-derived products, or graphite electrodes are frequently used in conventional synthesis pathways, these methods are energy-intensive and unsustainable for the environment. Agro-based residues have become a cheap, renewable, and carbon-rich substitute for CNT synthesis in recent years. This study summarizes the state of research worldwide on the use of typical agricultural wastes, such as rice hulls, coconut wastes, corn cobs, sugarcane bagasse, and palm leftovers, for the synthesis of carbon nanotubes. In addition to structural characterization approaches, the topic includes precursor properties and synthesis processes such pyrolysis, chemical activation, arc discharge, laser ablation, and selective chemical vapor deposition (CVD). Tables and schematic representations are used to help the comparative examination of the yields, structures, and properties of CNTs obtained from agriculture. Additionally highlighted are the uses of carbon nanotubes (CNTs) derived from biomass in the fields of biomedical, energy storage, environmental remediation, catalysis, and composites. Lastly, the paper discusses the present issues with consistency, scalability, and purification while providing guidance for future approaches to combining advanced nanomaterial production and biomass waste management.

Keywords: Carbon nanotubes, agro-residues, coconut wastes, rice hull, sugarcane bagasse, green nanotechnology, synthetic CVD, biomass valorization

1. Introduction

Iijima's 1991 learning of carbon nanotubes (CNTs) was a turning point in the study of nanomaterials (Iijima, 1991) [6]. Shaping graphene sheets into continuous tubes creates carbon nanotubes (CNTs), which are cylindrical forms of carbon with special physical, mechanical, electrical, and chemical characteristics (Dresselhaus *et al.*, 2001) [4]. CNTs are divided into two categories based on the construction of their walls: single-walled (SWCNTs) and multi-walled (MWCNTs). These substances have electrical characteristics that vary from conductive to semiconducting based on chirality, tensile strengths that surpass those of steel, and thermal conductivities that surpass those of diamond (Saito *et al.*, 2001) [12].

Even with these impressive qualities, industrial-scale CNT production is still difficult. Hydrocarbons derived from fossil fuels or graphite electrodes are commonly used in conventional techniques like arc discharge, laser ablation, and chemical vapor deposition (CVD) (Ando, 2010) [1]. These techniques are efficient, but they also take a lot of energy, emit greenhouse gases, and frequently include costly purification procedures.

A sustainable substitute is provided by feedstocks obtained from biomass, especially agro-based leftovers.

Environmental contamination is a result of the enormous volumes of lignocellulosic waste generated by agriculture each year, much of which is wasted or burned in the open (Gupta *et al.*, 2019) [5]. With different amounts of cellulose, hemicellulose, and lignin, these byproducts are rich in carbon and oxygen and are therefore good candidates for the synthesis of carbon nanotubes. A cheap and renewable resource basis is offered by common residues that are widely available throughout tropical and subtropical countries, including coconut wastes, husks from rice, bagasse from sugar cane, corn husks, and palm wastes (Kumar *et al.*, 2020) [8].

By concentrating on precursor chemical composition, synthesis techniques, product analysis, applications, and potential future study objectives, this review aims to present a thorough worldwide viewpoint on the production of carbon nanotubes (CNTs) from readily accessible agro-residues.

2. Agro-Residues as Carbon Precursors

The majority of agricultural residues are lignocellulosic, consisting of cellulose (35% to 50%), hemicellulose (20 to 35%), lignin (10 to 25%), and extractives and ash in different proportions. The amount of carbon, reactive matter, and mineral makeup all affect how well they work as carbon precursors.

2.1 Coconut Wastes

Hard, lignin-rich biomass leftovers with a low ash level and a high fixed carbon content (~52%), coconut wastes are ideal for the synthesis of carbon nanotubes (CNTs) (Rao *et al*., 2018) [11]. They have been effectively employed to produce CNTs with multi-walled systems by pyrolysis and chemically activated processes.

2.2 Rice Hulls

The distinctive feature of rice hulls is that they contain a considerable amount of silica (~15-20%) in along with carbon (~35-40%). According to Patel *et al*. (2019) [10], silica frequently serves as a naturally occurring catalyst for CNT synthesis, however a high ash level may reduce output. Generally speaking, CNTs made from rice husks exhibit favorable uniformity and dimension control.

2.3 Sugarcane Bagasse

This fibrous byproduct of the sugar industry, sugarcane bagasse, is high in cellulose (about 45%) and hemicellulose (about 28%). Because of its porous nature, it can be used with chemical activation techniques (Sharma *et al*., 2021) [13]. CNTs made from bagasse are renowned for their extensive surface area and adsorption power

2.4 Corn Cobs and Stalks

Worldwide, corn residues are plentiful and high in lignin and cellulose. Using catalysts made from transition metals such as Ni, Fe, or Co, studies have shown effective conversion into CNTs using catalytic CVD (Li *et al*., 2020) [9].

2.5 Palm Residues

In Southeast Asia, leftover oil palm fruit bundles and kernel hulls are easily accessible. CNTs derived from palm residue have attracted attention because to their fairly high stable carbon ratio and availability (Aziz *et al*., 2022) [2].

Table 1: Chemical composition of common agro-residues used for CNT synthesis

Residue type	Fixed carbon (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Key features for CNT synthesis
Coconut wastes	50-55	30-35	20-25	30-35	5-8	High fixed carbon, low ash
Rice hulls	35-40	35-40	15-20	20-25	15-20	Moderate carbon
Sugarcane bagasse	45-50	40-45	25-30	15-20	3-5	Porous structure, good for activation
Corn cobs/stalks	40-45	35-40	20-25	25-30	2-4	Abundant, good cellulose/lignin ratio
Palm residues	45-55	30-35	20-25	20-25	5-10	Widely available, tropical biomass

Table 2: Comparative yield chart of CNTs from different agro-residue

Agro-Residue	Synthesis Method	Yield
Coconut waste	Pyrolysis	Varies, can be high purity
Rice hulls	Pyrolysis (Catalytic)	Low-Moderate (<10%)
Sugarcane bagasse	Catalytic Pyrolysis Microwave-assisted Pyrolysis	Low-Moderate (<approx. 6%-8%) Varies, dependent on temperature
Corn cobs/stalks	Chemical Vapor Deposition (CVD)	Possible through various methods
Palm residues	Chemical Vapor Deposition (CVD)	Varies

3. Synthesis Techniques Using Agro-Residues

3.1 Pyrolysis

Biomass is heated to 400-900 °C in an inert atmosphere during the pyrolysis process. A carbon-rich char and volatiles are produced as the lingo cellulosic structure breaks down. CNT development during pyrolysis can be aided by transition metal catalysts. Rice husks and coconut shells work very well because of the significant carbon level (Singh *et al*., 2020) [14].

3.2 Synthetic Chemical Vapor Deposition (CVD)

The most widely used technique for agro-residue-derived CNTs is CVD. Decomposition of biomass releases volatiles that settle on metal catalysts (Ni, Fe,Co) based on silica or alumina. CNT diameter, quality, and orientation can all be controlled using this technique. According to Chen *et al*. (2018) [3], CVD is frequently used to synthesize CNTs derived from bagasse and maize cob.

3.3 Arc Discharge and Laser Ablation

Arc discharge and laser ablation can use carbons derived from biomass as electrodes, though this is less common. These processes produce CNTs of superior quality, but they are less scalable and require a lot of energy (Kumar & Sharma, 2017) [7].

3.4 Chemical Activation + Carbonization

Precursor porosity is increased by chemical activation with KOH, H_3PO_4, or $ZnCl_2$. Carbonization later on promotes the formation of CNTs. According to Tao *et al*. (2017) [15], CNTs with enhanced surface functional groups were produced from rice husks by using H_3PO_4.

Table 3: Comparison of synthesis techniques applied to agro-residues

Method	Temperature (°C)	Catalyst used	Advantages	Limitations
Pyrolysis	400-900	Fe, Ni, Co	Simple, scalable, low cost	Less control over CNT structure
Synthetic CVD	600-900	Ni, Co, Fe	Good control over diameter, yield	Requires catalyst preparation
Arc discharge	>2000	None	High-quality CNTs	High energy, low scalability
Laser ablation	>1200	Graphite target	High-purity CNTs	Expensive, small-scale
Chemical activation + carbonization	500-800	KOH, H_3PO_4	Enhanced porosity, functionalization	Risk of residual chemicals

4. Characterization of Biomass-Derived CNTs

- **SEM/TEM**: Morphological analysis shows CNT bundles, tubes, and porous carbon structures.
- **Raman spectroscopy**: D-band (~1360 cm^{-1}) and G-band (~1570 cm^{-1}) confirm graphitization.
- **FTIR**: Identifies surface functional groups (-OH,-COOH).
- **BET surface area**: Indicates porosity and adsorption potential.
- **XRD**: Confirms crystallinity and multi-walled nature.

5. Applications of Agro-Residue Derived CNTs

- **Environmental remediation**: Organic contaminants, heavy metals, and dyes are adsorbed (Gupta *et al.*, 2019) [5].
- **Energy storage**: Lithium-ion batteries and supercapacitor electrodes (Aziz *et al.*, 2022) [2].
- **Catalysis**: Fuel cells and chemical processes are aided by catalysts.
- **Biomedical applications**: Applications in biomedicine include medication administration following functioning and biosensors.
- **Composites**: Polymers and building materials reinforced mechanically.

Table 4: Applications of CNTs synthesized from agro-residues

Application area	Agro-residue precursor	CNT characteristics	Example use case
Environmental cleanup	Rice husks, bagasse	High porosity, surface groups	Dye removal, heavy metal adsorption
Energy storage	Coconut shells, corn cobs	High conductivity, surface area	Supercapacitor electrodes, Li-ion batteries
Catalysis	Palm residues, bagasse	Functionalized surfaces	Fuel cell catalysts
Biomedical	Rice husks, coconut shells	Functionalized CNTs	Biosensors, drug delivery
Composites	Corn stalks, palm residues	Multi-walled CNTs	Polymer reinforcement

6. Challenges and Future Perspective

6.1 Despite promising progress, several challenges hinder large-scale adoption

- **Yield optimization:** Highly dependent on feedstock variability.
- **Purification:** Removal of amorphous carbon and metal residues is necessary.
- **Scalability:** Most processes remain at laboratory scale.
- **Economic feasibility:** Cost-effectiveness versus petroleum-derived CNTs must be demonstrated.

6.2 Future directions

1. Development of low-cost, recyclable catalysts.
2. Hybrid use of multiple agro-residues to tune properties.
3. Integration of CNT synthesis into waste-to-energy systems.
4. Expansion into advanced applications such as green hydrogen, smart composites, and water purification.

7. Conclusion

An eco-friendly, plentiful, and renewable feedstock for CNT synthesis is provided by agro-residues. Corn cobs, sugarcane bagasse, coconut wastes, rice hulls, and palm leftovers have all demonstrated great promise as carbon precursors. With features similar to those obtained from traditional fossil-based precursors, the most practical synthesis methods are pyrolysis, selective CVD, and chemical activation.

Even though there are still issues with purification, scalability, and consistency, continuous research is moving in the right direction for industrial implementation. There is great potential for both advanced material production and sustainable waste management when agricultural residue utilization and nanotechnology come together.

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