

hemp-derived carbon nanosheets in bulk composite materials

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Hemp-derived carbon nanosheets (HDCNS) represent a groundbreaking advancement in sustainable materials science, offering a green alternative for high-performance bulk composite applications. These two-dimensional nanomaterials are distinguished by their exceptional mechanical, thermal, and electrical properties, akin to graphene but derived from a rapidly renewable biomass source. HDCNS are typically composed of a few to many layers of self-aligned, sp²-hybridized carbon atoms arranged in a hexagonal lattice structure. Their unique structure provides a high surface-to-volume ratio and mechanical robustness, making them ideal for enhancing various composite systems.

Historical Development and Significance of Hemp as a Precursor

The journey of carbon nanosheet production from hemp is rooted in the plant's long history of versatile applications, from ancient textiles to modern industrial uses. Hemp, or *Cannabis sativa* L.*, is a fast-growing, regenerative plant requiring minimal care, which makes it an ideal sustainable feedstock for carbon nanomaterial synthesis. A significant milestone occurred in 2013, when researchers demonstrated that waste hemp bast fibers could be processed to yield graphene-like carbon nanosheets through a combined hydrothermal and activation process. This pioneering work by Professor David Mitlin and colleagues at the University of Alberta showcased the potential for high-performance electrode materials for supercapacitors at a significantly reduced cost compared to conventional graphene. The inherent cellulose content of hemp, particularly in bast fibers, allows for the formation of well-ordered carbon frameworks with high crystallinity, making it a promising organic alternative to petroleum-based nanocarbons. The evolution of hemp-based nanotechnology has addressed limitations associated with expensive and complex synthesis methods of traditional carbon nanomaterials, paving the way for scalable and cost-effective production.

Synthesis and Processing Techniques for HDCNS

The production of hemp-derived carbon nanosheets involves several sophisticated synthesis and processing techniques, engineered to control their morphology and properties for specific applications. These methods are adaptable for both laboratory and industrial scales, ensuring scalability and economic feasibility.

Common Synthesis Methods

* Hydrothermal Carbonization (HTC) followed by Activation: This widely reported method begins with treating hemp fibers in hot water at elevated temperatures, typically around 180°C, in a sealed aqueous system. This initial step partially carbonizes the biomass and

dissolves non-cellulosic components like hemicellulose and lignin. The subsequent activation step, often employing chemical agents such as potassium hydroxide (KOH) or zinc chloride (ZnCl_2), is performed at high temperatures, usually between 700°C and 1000°C, in an inert atmosphere. This process significantly enhances the surface area and porosity, creating a rich network of micro and mesopores essential for high performance in supercapacitors and composites. The resulting nanosheets are typically 10–30 nanometers thick and are partially graphitic, possessing good electrical conductivity.

- * **Direct Pyrolysis:** This technique involves the thermal decomposition of hemp biomass in an inert atmosphere, such as nitrogen (N_2) or argon (Ar), at temperatures ranging from 500°C to 1000°C. This process can yield amorphous to semi-graphitic carbon nanosheets, with properties influenced by parameters like heating rate, hold time, and biomass particle size. Pyrolysis of folic acid, for instance, can result in porous carbon nanosheets around 900 nm thick. The method is straightforward, cost-effective, and does not require environmentally harmful surfactants or toxic chemicals.

- * **Chemical Activation:** This technique often involves impregnating hemp biomass with activating agents like KOH or ZnCl_2 before pyrolysis, leading to high surface area nanosheets with increased conductivity. Phosphoric acid activation at a carbonization temperature of 400°C has also been used to prepare activated carbon from hemp fibers.

Emerging and Advanced Techniques

- * **Microwave-Assisted Pyrolysis:** This method offers rapid and uniform heating, which can enhance graphitization at lower temperatures, leading to more efficient production.

- * **Plasma Treatment:** Plasma treatment is used for surface functionalization of nanosheets with oxygen or nitrogen groups, which can improve their dispersion in polymer matrices and enhance interfacial bonding.

- * **Template-Assisted Activation:** This approach uses sacrificial templates (e.g., MgO, silica) to precisely control the dimensions and morphology of the nanosheets, with the template removed post-carbonization using acid washing.

These methods collectively enable the tailoring of HDCNS properties, including pore structures, graphitization degree, and surface functionalities, which are crucial for optimizing their performance in various composite applications.

Properties of Hemp-Derived Carbon Nanosheets

HDCNS exhibit a unique combination of physical, chemical, electrical, thermal, and mechanical properties, making them highly versatile for advanced composite materials.

Physical Properties

The morphology of HDCNS is typically described as an interconnected network of partially graphitic structures. Electron microscopy images reveal sheet-like structures that tend to scroll and wrinkle, contributing to an ultra-high surface area. Biochars, in general, are characterized by their porous nature and large surface area, with HDCNS demonstrating specific surface areas up to 2287 m^2/g , especially after activation. They also exhibit significant mesoporosity,

often reported to be up to 58% or centered at 3.0-4.5 nm after hydrothermal processing and activation. The thickness of these nanosheets can vary, commonly reported in the range of 10 to 30 nm. When derived from hemp fibers through pyrolysis, they can even retain their original fibrous morphology.

Chemical Properties

HDCNS are primarily composed of carbon, with the presence of oxygen and nitrogen depending on the synthesis conditions and original feedstock. Techniques like X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) are employed to identify surface functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O/C-C) groups. These surface functionalities are critical for the material's interaction with other substances, particularly the matrix in composite materials. HDCNS also demonstrate high thermal stability, capable of withstanding temperatures approaching 1000°C.

Electrical and Thermal Conductivity

HDCNS possess excellent electrical conductivity, with reported values ranging from 211 S/m to 226 S/m for interconnected partially graphitic carbon nanosheets derived from hemp bast fiber. This conductivity is attributed to the evolution of the biochar microstructure, including the development of graphite-like structures during high-temperature carbonization. Even though they might not be as conductive as pristine graphite, they are significantly more conductive than state-of-the-art activated carbon. Regarding thermal conductivity, while less prevalent in literature for intrinsic HDCNS, biochar in general can contribute positively to the thermal properties of composites. Their two-dimensional structure allows for efficient propagation of thermal energy, with values comparable to other carbon-based materials like graphene.

Mechanical Properties

The mechanical properties of HDCNS are crucial for their role as reinforcing agents in composites. While direct measurements for the nanosheets themselves are not consistently available, their high tensile strength, exceptional durability, and impressive flexibility have been highlighted. These characteristics translate into significant performance enhancements when incorporated into composite matrices. For instance, hemp fibers themselves have reported tensile strength values from 97.33 MPa to 1110 MPa and Young's modulus values between 3.77 GPa and 92.44 GPa. Incorporating biochar into polyvinyl alcohol composites has shown an increase in tensile modulus and storage modulus. The ability of HDCNS to bend, twist, and deform without breaking makes them highly versatile for various applications, including defense.

Integration into Bulk Composite Materials

Effective integration of hemp-derived carbon nanosheets into bulk composite materials requires careful consideration of dispersion strategies, matrix compatibility, and interfacial engineering approaches to maximize performance.

Dispersion Strategies

Achieving uniform dispersion of HDCNS within a composite matrix is a critical challenge due to their tendency to agglomerate via van der Waals forces. Various techniques are employed to overcome this, including mechanical and chemical methods.

- * **Mechanical Exfoliation and Mixing:** Ball milling or sonication can exfoliate pyrolyzed hemp biochar to control nanosheet thickness and lateral size, aiding dispersion. High shear mixing and calendaring are common for dispersing nanoreinforcements in viscous polymer matrices.
- * **Chemical Functionalization:** Attaching different functional groups (e.g., hydroxyl and carboxylic acid groups) to the surface of carbon nanoparticles prevents aggregation due to their large size and strong dipole–dipole intermolecular forces. This also helps in dispersing the nanosheets evenly in both hydrophobic and hydrophilic solvents, and within the polymer matrix. Supercritical water treatment, for example, can activate various functional groups on the nanosheet surface, enhancing dispersion.
- * **Surfactant and Polymer Additives:** The use of surfactants or nanocellulose, especially those with high surface charge density, can stabilize carbon nanomaterial dispersions in aqueous media without the need for additional chemical functionalization.

Matrix Compatibility

The performance of HDCNS composites largely depends on the chemical affinity between the nanosheets and the matrix. Hemp fibers, being hydrophilic, often require surface modification to improve compatibility with hydrophobic polymer matrices.

- * **Surface Treatments:** Chemical treatments like alkali treatment (mercerization), acrylation, acetylation, and silane treatment are widely used to enhance the properties of hemp fibers and their composites. Alkali treatment, involving NaOH solution, reacts with hydroxyl groups in amorphous regions, reducing hydrophilicity and exposing short-length crystallites for better compatibility.
- * **In-situ Polymerization:** This method involves the dispersion of carbon nanofillers within the polymer matrix during the polymerization process, promoting better integration.
- * **Compatibility with Various Polymers:** HDCNS are compatible with biopolymers like polylactic acid (PLA) and polyhydroxybutyrate (PHB), and synthetic resins such as epoxy and polyurethane. They are also explored in thermoset and thermoplastic polymer matrices, including high-density polyethylene, polypropylene, polystyrene, and polyesters.

Interfacial Engineering Approaches

Strengthening the interface between HDCNS and the matrix is achieved through various techniques that enhance load transfer and overall composite performance.

- * **Functional Group Introduction:** The incorporation of functional groups on the nanosheet surface can increase electrical conductivity, tensile strength, and capacity, and enable the production of new polymer nanocomposites.
- * **Nanoparticle Anchoring:** Anchoring metal or metal oxide nanoparticles onto the carbon nanosheets can improve interfacial interactions and introduce new functionalities like catalytic activity.
- * **Conductive Networks:** The formation of a conductive network by HDCNS within the matrix

enhances electrical conductivity and allows for improved dissipation of electromagnetic energy through mechanisms like electron migration and hopping.

Resulting Composite Properties

The integration of HDCNS profoundly impacts the properties of bulk composites.

- * **Mechanical Enhancement:** Incorporating pyrolyzed hemp fibers into an epoxy matrix significantly increases the storage modulus, indicating a reinforcing effect. Hemp fiber-reinforced polymer composites exhibit satisfactory mechanical properties, including high strength and stiffness. The addition of a small amount of nano-inorganic fillers, typically less than 5 wt%, can bring about considerable improvement in mechanical properties due to the large surface area to volume ratio of fillers.
- * **Electrical Conductivity:** HDCNS incorporation leads to a significant increase in electrical conductivity in composites. For instance, composites containing 10 wt% hemp-derived carbon fibers reached 6 mS/m. Reduced graphene oxide (RGO) composites, with a conductivity of 64 S/m at 2.7 vol% RGO, demonstrate the potential for conductive polymer nanocomposites.
- * **Thermal Properties:** HDCNS can enhance thermal conductivity and stability. For example, polyamide-6/exfoliated graphite composite reached a thermal conductivity of $4 \text{ Wm}^{-1} \text{ K}^{-1}$ at 20 vol% graphite loading, compared to $0.25 \text{ Wm}^{-1} \text{ K}^{-1}$ for control polyamide-6.
- * **Tribological Behavior:** Hemp-derived carbon fibers can improve the wear resistance of epoxy resins, resulting in lower friction coefficients and wear rates.

Applications of HDCNS Composites

Hemp-derived carbon nanosheet composites are being explored across diverse industrial sectors, driven by their unique properties and sustainability benefits.

Energy Storage

HDCNS are revolutionizing energy storage solutions, particularly in supercapacitors and batteries.

- * **Supercapacitors:** Hemp-derived carbon nanosheets serve as highly efficient electrode materials for supercapacitors due to their high specific surface area and excellent electrical conductivity. These supercapacitors offer ultra-fast charge/discharge behavior, high specific capacitance (up to 103 F g^{-1}), and excellent cycle life (more than 10^4 cycles), outperforming commercial counterparts. They can also operate under wider temperature margins, from 0°C to 100°C , and provide high energy densities up to 12 Wh/kg , which is two to three times higher than commercially available supercapacitors.
- * **Batteries:** HDCNS are explored as anode materials for lithium-ion and sodium-ion batteries, showing promising potential due to their sustainable nature and scalable production.

Automotive Industry

HDCNS composites are highly attractive for the automotive sector due to their lightweight and high-strength properties. They contribute to manufacturing lighter, more fuel-efficient

vehicles, which in turn helps reduce greenhouse gas emissions. Hemp fiber-reinforced polymer composites were historically used in the body of a Henry Ford automobile in 1941, demonstrating early potential for impact resistance. Germany has been a leader in incorporating natural fibers into automotive composites, and the market share of natural fiber-reinforced composites in the EU's automotive sector grew significantly.

Aerospace Industry

The aerospace industry benefits from HDCNS composites for their ability to create lightweight and durable components for aircraft and spacecraft. The high strength-to-weight ratio and excellent dimensional stability make them ideal for structural and non-structural applications in this sector. Epoxy/CNT nanocomposites, for example, are used in aerospace engineering due to their thermal resistance and high specific strength, with HDCNS offering similar benefits as reinforcements.

Construction

In the construction sector, hemp-derived carbon nanosheets enhance the performance and durability of building materials like concrete and other bio-based panels. Hemcrete, a material made from hemp hurd, lime, and water, offers high thermal efficiency and has strong claims to being carbon negative, making it an environmentally friendly alternative.

EMI Shielding

HDCNS composites provide effective electromagnetic interference (EMI) shielding capabilities due to their excellent electrical conductivity. Composites of Fe_3O_4 nanoparticles on carbonized hemp fibers have demonstrated excellent microwave absorption performance, covering entire X-band (8–12 GHz) and Ku-band (12–18 GHz) frequencies, making them promising for electromagnetic protection.

Environmental Applications

Hemp-derived carbon nanosheets have significant potential in environmental applications, including water and air purification, and carbon capture technologies. Their high surface area and porosity make them effective in filtering contaminants from water and removing pollutants from air. Furthermore, HDCNS can be utilized in technologies designed to capture and store carbon dioxide, contributing to climate change mitigation.

Sensors and Flexible Electronics

The excellent electrical conductivity and flexibility of HDCNS make them suitable for use in flexible electronic devices, sensors, and wearable technology. Graphene-based nanoparticles, similar to HDCNS, have been used in various imaging and sensing applications due to their versatile surface functionalization and high surface area.

Comparative Analysis with Other Carbon Nanomaterials

HDCNS offer a compelling alternative or complement to traditional carbon nanomaterials like graphene and carbon nanotubes (CNTs) in composite applications.

HDCNS vs. Graphene

- * **Cost and Sustainability:** A primary advantage of HDCNS is their significantly lower production cost, estimated at \$500 to \$1,000 per tonne, which is about one-thousandth the cost of graphene. This is due to hemp being an inexpensive, fast-growing renewable resource, unlike graphene, which often requires costly mining of graphite and complex, polluting chemical processes.
- * **Performance:** While graphene possesses exceptional mechanical (tensile strength up to 130 GPa, Young's modulus 1.0 TPa) and electrical properties (around 2×10^5 S/m), HDCNS offer comparable performance in terms of energy storage and reinforcement at a fraction of the cost. The crumpled and porous morphology of hemp-derived nanosheets can even be beneficial for supercapacitor electrodes by preventing stacking and increasing accessible surface area, addressing a common limitation of pristine graphene.
- * **Ease of Processing:** Hemp-derived nanosheets are often easier to process due to their inherent structural characteristics.

HDCNS vs. Carbon Nanotubes (CNTs)

- * **Structure and Properties:** CNTs are one-dimensional tubular structures with exceptional tensile strength (50–250 GPa) and Young's Modulus (1.0 TPa), offering excellent electrical and thermal conductivity. HDCNS, on the other hand, are two-dimensional nanosheets.
- * **Synergy in Hybrid Composites:** Hybrid composites combining HDCNS (or hemp fibers) with CNTs can yield superior performance by leveraging the distinct advantages of each material. For example, the addition of carbon nanotubes to hemp/vinyl ester/carbon fiber laminated hybrid composites has been shown to improve mechanical properties significantly. A high-performance fiber-shaped electrode using hierarchical NiCo_2O_4 @polypyrrole core-shell nanowires on hemp-derived carbon microfibers demonstrates ultrahigh specific capacitance.
- * **Dispersion:** Like HDCNS, CNTs also face challenges in achieving homogeneous dispersion within polymer matrices due to their tendency to entangle.

Overall Advantages and Limitations of HDCNS

- * **Advantages:** HDCNS are sustainable, cost-effective, and derived from an abundant renewable resource. They possess high specific surface area, excellent electrical conductivity, and good mechanical properties, making them competitive with or superior to other carbon nanomaterials in certain applications, especially energy storage.
- * **Limitations:** Challenges remain in achieving optimal uniform dispersion of HDCNS within highly viscous polymer matrices to prevent agglomeration and fully realize their potential. The quality and consistency of HDCNS can also vary depending on the specific synthesis conditions and feedstock variability.

Scalability and Economic Feasibility

The production of hemp-derived carbon nanosheets for bulk composite manufacturing is highly scalable and economically feasible, presenting a significant advantage over many

conventional nanomaterials.

Production Costs and Comparison

The cost-effectiveness of HDCNS is a major driving factor for their adoption. Production costs are estimated to be between \$500 and \$1,000 per tonne, significantly lower—approximately one-thousandth—than that of graphene. This substantial cost reduction is largely attributed to the low cultivation and processing costs of hemp, a fast-growing plant that requires minimal inputs.

Supply Chain Considerations

The industrial hemp industry is characterized by its robust and increasingly established supply chain, which supports the consistent availability of raw materials for HDCNS production. Hemp is cultivated globally, with growing interest and legalization trends further boosting its supply. The use of waste hemp fibers as a starting material, which are often by-products of other hemp industries, further enhances the economic viability by valorizing waste streams.

Environmental and Sustainability Aspects

The use of hemp-derived carbon nanosheets in composites offers significant environmental and sustainability benefits, aligning with principles of circular material economies.

Life Cycle Assessment (LCA) and Carbon Footprint

Hemp cultivation is inherently sustainable, growing quickly with minimal resource requirements such as pesticides and fertilizers. It is a strong carbon sequester, capable of capturing large amounts of CO₂ per acre, more than most plants, thus helping to mitigate climate change. LCAs consistently show that hemp-based materials, including those derived from hemp straw, hemp hurd, and hemp fiber, have a lower environmental footprint compared to conventional materials. This makes HDCNS composites potentially carbon-negative, effectively acting as carbon sinks.

End-of-Life Considerations

Hemp-derived composites generally offer improved end-of-life options compared to synthetic counterparts. Hemp fibers are biodegradable, and the composites can be designed for recyclability. While carbonized nanosheets themselves pose similar recycling challenges to other carbon materials, ongoing research into the recovery of carbon fibers from polymeric composite waste is advancing. The ability to use hemp as a sustainable precursor helps reduce reliance on harmful synthetic materials, decreasing overall pollution and waste.

Regulatory, Safety, and Standardization Issues

While the potential of HDCNS is vast, their widespread adoption hinges on addressing complex regulatory, safety, and standardization issues.

Regulatory Landscape for Hemp

The cultivation and processing of industrial hemp are subject to varying legal frameworks globally, impacting the consistency and availability of raw materials. Regulatory bodies dictate aspects like licensing, permitted hemp varieties, and allowable cannabinoid (e.g., THC) concentrations. These regulations directly influence the quality and safety of the hemp biomass used for nanosheet production. Establishing clear, international regulatory frameworks and guidelines is crucial for ensuring product safety, quality, and consumer trust.

Safety Considerations for Nanomaterials

The handling and manufacturing of nanomaterials like HDCNS require careful consideration of potential health hazards, particularly inhalation risks during production and processing. Adherence to stringent industrial hygiene practices and the implementation of appropriate protective measures are essential to mitigate these risks.

Standardization Challenges

Achieving consistent quality in HDCNS, regarding their thickness, purity, and defect density, is a significant challenge that impacts composite performance. Developing standardized quality metrics, testing methods, and product labeling protocols is vital for batch-to-batch consistency and widespread market acceptance. This includes standardizing methods for characterization techniques such as X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) to ensure reliable data on composition, crystallinity, and morphology.

Future Trends and Research Directions

The field of hemp-derived carbon nanosheet composites is dynamic, with future trends focusing on advanced production, diversified applications, and overcoming existing challenges.

Optimization of Synthesis and Properties

Ongoing research aims to further optimize efficient, low-energy synthesis techniques to precisely tailor the nanosheet morphology and properties. This includes refining hydrothermal carbonization and chemical activation methods to yield materials with enhanced characteristics, as well as exploring novel approaches such as catalytic carbonization. Emphasis is placed on engineering interfacial bonding to maximize load transfer and functional performance within composite matrices.

Expansion of Applications

Future research will continue to expand the application domains of HDCNS composites. This includes continued development in:

- * Multifunctional Composites: Exploring advanced functionalities such as smart materials, self-healing composites, and materials with integrated sensing capabilities.
- * Bio-composites and Green Plastics: Developing fully organic matrices reinforced with HDCNS to yield biodegradable, high-performance materials for construction panels,

packaging, and automotive interiors.

- * Next-Generation Energy Storage: Advancements in supercapacitors and batteries, including solid-state devices, with higher energy and power densities, and improved cycle stability across broader temperature ranges.
- * Environmental Remediation: Expanding their use in water and air purification, and exploring new avenues for carbon capture and conversion technologies.

Addressing Technological Challenges

Key challenges that research endeavors will address include:

- * Uniform Dispersion: Developing robust and scalable methods to achieve homogeneous dispersion of nanosheets in highly viscous polymer matrices to prevent agglomeration.
- * Quality Consistency: Ensuring batch-to-batch consistency in nanosheet quality, morphology, and functional properties during large-scale production.
- * Balancing Properties: Optimizing the trade-off between various properties such as electrical conductivity, mechanical strength, and cost-effectiveness while maintaining sustainability.

The advent of global hemp legalization, as envisioned in the "Hemp Rush of the 2020s," is expected to further accelerate innovation and commercialization of hemp-derived carbon nanosheet composites, driving significant economic and environmental opportunities.

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