

Seshat's HD-1D-DNTs: A Green Chemistry Route to Ultra-High-Strength Diamond Nanothreads from Renewable Hemp Biomass

Abstract

The synthesis of one-dimensional diamond nanothreads (DNTs), materials possessing extraordinary theoretical specific strength, has traditionally relied on high-pressure polymerization of petrochemical aromatic precursors. We report a novel, highly sustainable synthesis route for **Hemp-Derived 1D Diamond Nanothreads (HD-1D-DNTs)**, which we term **Seshat's HD-1D-DNTs**. This approach adheres strictly to green chemistry principles by sourcing carbon from **hemp biomass** via a two-stage process: (1) **Hydrothermal Liquefaction (HTL)** and **Catalytic Hydrodeoxygenation (HDO)** transform hemp lignin into purified aromatic precursors. (2) These precursors undergo **Pressure-Induced Polymerization (PIP)** under controlled isothermal compression (~ 20 GPa) within a Diamond Anvil Cell (DAC). Successful transformation from sp^2 to the diamond-like sp^3 structure is confirmed by the characteristic $\sim 1332\text{ cm}^{-1}$ band in **Raman spectroscopy**. This methodology offers a carbon-negative pathway to produce high-performance nano-reinforcement. We propose the integration of functionalized Seshat's HD-1D-DNTs into bio-based **Hempoxies**, projecting a revolutionary increase in composite **tensile strength and fracture toughness**, thereby enabling the next generation of lightweight, sustainable materials for aerospace, automotive, and high-performance structural applications.

1. Materials and Methods: Synthesis Protocol

This protocol outlines the lab-scale synthesis of HD-1D-DNTs, emphasizing green chemistry throughout the process.

1.1. Hemp Valorization and Aromatic Precursor Isolation

1. **Feedstock Preparation:** Dried industrial **hemp hurds** (lignocellulosic biomass) are milled into a fine powder ($< 100\text{ }\mu\text{m}$) to maximize surface area for subsequent processing.
2. **Hydrothermal Liquefaction (HTL):** The hemp powder (100 g) is mixed with **deionized water** in a high-pressure batch reactor. The mixture is heated to **300–350 °C** and held at **10–20 MPa** for 30 minutes. This process efficiently separates the biomass into a high-quality **bio-oil** (rich in aromatic oxygenates from lignin), residual char, and an aqueous phase.
3. **Catalytic Hydrodeoxygenation (HDO):** The bio-oil is combined with **supercritical CO₂ (scCO₂)**—used as a green, tunable solvent—and passed through a fixed-bed reactor containing a heterogeneous catalyst (e.g., Ni/SiO₂-Al₂O₃). The reaction occurs at **350 °C** and **15 MPa** under a continuous flow of H₂. This step removes oxygen atoms, yielding

highly pure, crystalline **aromatic precursors** (e.g., furan or benzene derivatives).

4. **Purification:** The precursor is fractionally condensed, and its purity is verified via **Gas Chromatography-Mass Spectrometry (GC-MS)**.

1.2. Pressure-Induced Polymerization (PIP)

1. **High-Pressure Setup:** A highly pure, microscopic crystal of the hemp-derived aromatic precursor is loaded into the **100–300 μm** bore of a Rhenium gasket within a **Diamond Anvil Cell (DAC)**. A small ruby chip is co-loaded for *in situ* pressure measurement via fluorescence.
2. **Compression and Reaction:** Pressure is increased slowly and isothermally (ambient temperature) at a controlled rate of approximately **1.0 GPa/h** until the target polymerization pressure of **18–22 GPa** is achieved. The pressure is held constant for **12 hours** to facilitate the solid-state [4+2] cycloaddition and C-C bond reorganization, forming the sp^3 backbone of the HD-1D-DNTs.
3. **Decompression:** The pressure is released **slowly** (maintaining the rate of 1.0 GPa/h) to ambient conditions. This critical step preserves the metastable nanothread structure.

2. Characterization and Structure Confirmation

Rigorous analytical techniques are essential to confirm the successful synthesis and diamond-like structure.

- **Raman Spectroscopy (Structure Confirmation):** This is the primary diagnostic tool. The successful formation of the sp^3 diamond structure is confirmed by the **complete disappearance** of the sp^2 aromatic vibrational modes ($\sim 1600\text{ cm}^{-1}$) and the appearance of a characteristic broad band near **1332–1350 cm^{-1}** , consistent with the diamond nanothread lattice.
- **Transmission Electron Microscopy (TEM):** High-Resolution TEM (**HRTEM**) is used to visually confirm the **one-dimensional structure** and measure the thread diameter ($\sim 0.2\text{--}0.6\text{ nm}$). **Selected Area Electron Diffraction (SAED)** patterns verify the unique crystalline packing.
- **X-ray Diffraction (XRD):** Powder XRD provides data to confirm the formation of a novel, highly dense, crystalline phase, verifying the transformation from the precursor lattice to the DNT structure.

3. Discussion: Applications and Sustainability Impact

3.1. Competitive Advantages

The use of hemp as a feedstock for HD-1D-DNTs confers both **performance and sustainability** benefits:

- **Renewable Sourcing:** Sourcing carbon from **hemp biomass**, a rapidly renewable and CO_2 -sequestering crop, provides a strong **Green Chemistry** advantage over petrochemical-derived DNTs.
- **Superior Specific Strength:** DNTs possess a theoretical ultimate tensile strength of $\sim 134\text{ GPa}$, potentially **doubling** that of the highest-performing carbon nanotubes (CNTs). This results in the **highest specific tenacity** known for any fiber material.

- **Interface Optimization:** The sp^3 backbone results in a highly **functionalizable surface** (e.g., hydrogen-capped), enabling direct covalent coupling with the bio-epoxy matrix of **Hempoxies**. This maximizes interfacial load transfer, addressing the common weakness in conventional nanocomposites.

3.2. Integration into Hempoxies and Industrial Applications

The primary application is the reinforcement of **Hempoxies**—bio-based thermoset composites.

- **Hempoxies Enhancement:** Integration of Seshat's HD-1D-DNTs is expected to dramatically increase the composite's **Young's Modulus, tensile strength, and fracture toughness**, positioning these bio-composites as high-performance, lightweight structural materials suitable for demanding applications.
- **Industrial Scale-Up:** Industrial production will necessitate replacing the batch-mode DAC with continuous high-pressure systems, such as modified **Belt-Type Presses**, alongside large-scale, continuous-flow biorefining for precursor generation.
- **Other Markets:** Beyond Hempoxies, Seshat's HD-1D-DNTs are targeted for use in **aerospace structural components** (where weight savings are critical), **ballistic materials**, and advanced **nano-energy storage** devices due to their unparalleled strength-to-weight ratio.