



Drying-controlled internal structure for enhanced post-treatment efficiency in high-strength carbon nanotube fibers

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ABSTRACT

Mechanical failure in carbon nanotube fibers (CNTFs) is primarily governed by inter-bundle slippage due to weak van der Waals interactions; thus, placing covalent crosslinks at bundle–bundle interfaces is critical for reinforcement. However, conventional functionalization approaches offer limited spatial control over crosslinking within the hierarchical fiber structure. Here, we demonstrate a wet-state engineering strategy that exploits the drying process during CNTF fabrication to regulate crosslinking-reagent infiltration and thereby target specific crosslinking sites. Electrochemically active surface area (ECSA) measurements confirmed that reagent-accessible CNT surface area decreases with increasing drying degree, demonstrating that internal reagent accessibility is governed by drying state. In wet CNTFs, extensive reagent penetration yields broadly distributed functionalization rather than targeted interfacial reinforcement. In fully dried fibers, severe densification and hydrophobic recovery restrict reagent access to the outer region. Partially dried fibers, however, allow reagents to reach inter-bundle regions, promoting covalent bridging precisely where load transfer is most limited. Consequently, crosslinked partially dried CNTFs (c-pd-CNTF) showed the highest reinforcement, with specific tensile strength and stiffness reaching 146% and 160% of pristine CNTFs (p-CNTF), respectively. In situ Raman analysis revealed the highest G' peak shift rate of $25.2\text{ cm}^{-1}/\%$ for c-pd-CNTF, confirming superior load transfer efficiency. Furthermore, c-pd-CNTF retained mechanical performance under water and isopropyl alcohol (IPA) exposure and exhibited superior knot strength and dynamic work recovery. These findings establish drying-state control as a critical structural design parameter governing CNTF microstructure, reagent accessibility, and post-treatment efficiency.

1. Introduction

High-strength and high-conductivity carbon nanotube fibers (CNTFs) have attracted considerable attention as next-generation materials for advanced composites and energy applications [1,2], owing to their superior mechanical and electrical properties combined with a much lower density compared to metals and ceramics [3–6]. Recent studies have reported CNTFs with specific mechanical properties comparable to or exceeding those of high-performance fibers such as carbon fibers and Kevlar [7], and their hybridization with copper has further demonstrated potential for use as ultralight, high-conductivity wiring materials [8,9]. CNTFs are typically fabricated through a fiber-spinning

process that assembles individual CNTs into macroscopic structures [10], followed by post-treatment processes [11]. The mechanical properties of CNTFs are strongly dependent not only on the intrinsic structure of the constituent CNTs but also on their hierarchical assembly, including alignment [12], bundle packing [13], and interfacial interactions [14]. In particular, a high degree of CNT alignment along the fiber axis plays a crucial role in enhancing tensile strength, as it enables more efficient stress transfer between adjacent CNTs [15]. According to classical fiber mechanics, the effective load-bearing contribution of a fiber decreases with the cosine of the orientation angle (θ) relative to the loading direction [16]. Therefore, aligning CNTs along the fiber axis by controlling the winding speed during spinning or by applying

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post-drawing processes is an effective strategy for improving the tensile strength of CNTFs. Indeed, Vilatela et al. [17] demonstrated that optimizing the winding speed during fabrication enhances CNT alignment, while Kim et al. [18] reported that post-drawing treatments can significantly improve the mechanical performance of CNTFs. However, the failure of CNTFs is still generally governed not by the fracture of individual CNTs but by intertube slippage, due to the relatively weak van der Waals interactions between CNTs compared to the strong sp^2 covalent bonds within each nanotube [19]. To overcome this limitation, numerous strategies have been explored to introduce stronger intertube interactions through ionic [20], metallic [21], or covalent bonding [22]. Although physical approaches based on structural control and chemical approaches based on intertube bonding have each been actively investigated to enhance CNTF strength [23,24], their mutual relationship and synergistic effects have rarely been addressed. Interestingly, some recent works have suggested that selective formation of chemical bonds—particularly on CNT bundle surfaces or in highly aligned regions—can lead to more substantial improvements in tensile strength [25]. These findings suggest that structural factors play a critical role in determining the efficiency and spatial distribution of post-treatment reactions, which ultimately govern the mechanical performance of CNTFs. Therefore, understanding how the fiber fabrication process influences the internal structure and surface characteristics of CNTFs is essential. In this study, we focus on the drying process, an inevitable step in CNTF fabrication, to elucidate how the degree of drying affects CNT bundling behavior and the formation of intertube chemical bonds, and consequently, the mechanical properties of the fibers. Through this investigation, we aim to provide deeper insights into the processing–structure–property relationships in CNTF systems.

2. Experimental

2.1. Fabrication of carbon nanotube fibers (CNTFs)

CNTFs were fabricated via a direct spinning method [26]. Ferrocene and thiophene were employed as the catalyst precursor and co-catalyst, respectively, while methane gas was used as the carbon source. A mixture of hydrogen and argon served as the carrier gas. Ferrocene and thiophene were purchased from Sigma-Aldrich Korea and used without further purification or treatment. All gases used in the process had a purity of 99.999%. The precursor materials and gases were introduced into the reactor, maintained at 1200 °C, where CNT growth occurred. Inside the reactor, the synthesized CNTs formed a continuous interconnected network, resulting in an aerogel structure that exited the reactor outlet. The as-grown CNT aerogel was then passed through a water bath to condense into a continuous macroscopic fiber, which was collected by a winder. The obtained CNTFs were stored by immersing the wound bobbins in water to prevent drying.

2.2. Drying process

A schematic illustration of the sample preparation routes, including the pristine fiber (p-CNTF) and the different drying conditions applied prior to crosslinking, is shown in Fig. S1. For the pristine fibers (p-CNTF), as-spun fibers stored in water were transferred into acetone while still wound on the bobbin. A single fiber was then unwound from the acetone bath and dried in air under ambient conditions. For the wet CNTFs (w-CNTF), the fibers remained immersed in water until immediately before being transferred into the crosslinking reaction solution. For the partially dried CNTFs (pd-CNTF), fibers were removed from water and air-dried under ambient conditions for 24 h. For the fully dried CNTFs (fd-CNTF), fibers were removed from water and dried under vacuum at 80 °C for 24 h. The dried fibers were then subjected to the crosslinking process. After crosslinking, the fibers were immersed in acetone and subsequently dried using the same procedure as that used for p-CNTF.

2.3. Chemical crosslinking

Covalent crosslinking was performed in a two-step process using diazonium ions. In the first step, CNTFs prepared under each drying condition were subjected to diazonium functionalization at 50 °C for 4 h in an acidic aqueous solution containing 0.24 M sodium nitrite (NaNO_2 , Sigma-Aldrich), 0.30 M 4-aminobenzoic acid (PABA, Sigma-Aldrich), and 1 M hydrochloric acid (HCl, Samchun Chemicals), thereby introducing carboxylic acid groups onto the CNT surfaces. Subsequently, the functionalized CNTFs were washed three times each with N,N-dimethylformamide (DMF, Samchun Chemicals) and acetone (Samchun Chemicals) for 5 min per cycle. The washed CNTFs were then immersed in a 0.1 mM aqueous solution of Jeffamine ED-2003 (O,O-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol, Sigma-Aldrich) (dissolved in deionized water) and reacted at 95 °C for 24 h to induce covalent crosslinking. Finally, the crosslinked fibers underwent the identical washing procedure and were subsequently dried.

2.4. Characterization

The morphology and diameter of the CNTFs were observed using optical microscopy (OM, ECLIPSE LV 150 N, Nikon). The fracture surfaces of the fibers were analyzed via field emission scanning electron microscopy (FE-SEM, S-8220, Hitachi). For the observation of the number of CNT walls, cross-sectional samples were prepared using a focused ion beam (FIB, Helios NanoLab G3 UC, FEI) and subsequently imaged with field emission transmission electron microscopy (FE-TEM, HF-3300, Hitachi). Water contact angle measurements were performed using a drop shape analyzer (DSA 100, Krüss). Thermogravimetric analysis (TGA, TGA 55, TA Instruments) was conducted in air and argon at a heating rate of 10 °C min^{-1} . Electrochemical measurements were performed using a potentiostat (Biologic VSP-300) in a three-electrode system with a Pt mesh counter electrode, an Ag/AgCl reference electrode, and CNTF as the working electrode. Electrochemical double-layer capacitance was measured by stabilizing the open-circuit potential (OCP) for approximately 100 s, followed by recording CV scans at scan rates of 5, 10, 20, 30, 40, and 50 mV/s over a range of ± 50 mV of the OCP. Functional group analysis was performed using Fourier transform infrared spectroscopy (FT-IR, Nicolet iN10MX, Thermo Fisher Scientific). The crystallinity and polarized Raman spectra were measured using Raman spectroscopy (ARI, WEVE), while the surface chemical composition of the CNTFs was analyzed via X-ray photoelectron spectroscopy (XPS, Nexsa G2, Thermo Fisher Scientific). Tensile and cyclic loading tests were performed using a single-fiber tester (Textechno FAVIMAT+, Germany) at a gauge length of 20 mm and a crosshead speed of 2 mm min^{-1} . Cyclic loading tests were conducted for 10 cycles at 80% of the maximum load. In situ Raman spectroscopy was conducted utilizing a high-resolution Raman spectrometer (LabRAM HR, Horiba Jobin Yvon SAS) equipped with a tensile stage (TST350, Linkam).

3. Results and discussion

3.1. Effect of drying on structural evolution of CNTFs

CNTFs synthesized by the floating catalyst chemical vapor deposition (FCCVD) method mainly consist of double-walled carbon nanotubes (DWCNTs) and exhibit high purity, containing only 6% residual catalyst even in the absence of post-purification steps (Fig. S2). A schematic representation of the bundling behavior and the proposed crosslinking distribution as a function of drying conditions is presented in Fig. 1. As-prepared wet fibers (w-CNTF) exhibit a hydrogel-like state containing a large amount of interstitial water within the CNT bundle network, as shown in Fig. 1a. During partial drying (pd-CNTF), free water near the fiber surface is preferentially removed, while a limited amount of residual water can remain trapped within confined inter-bundle regions

Data will be made available on request.

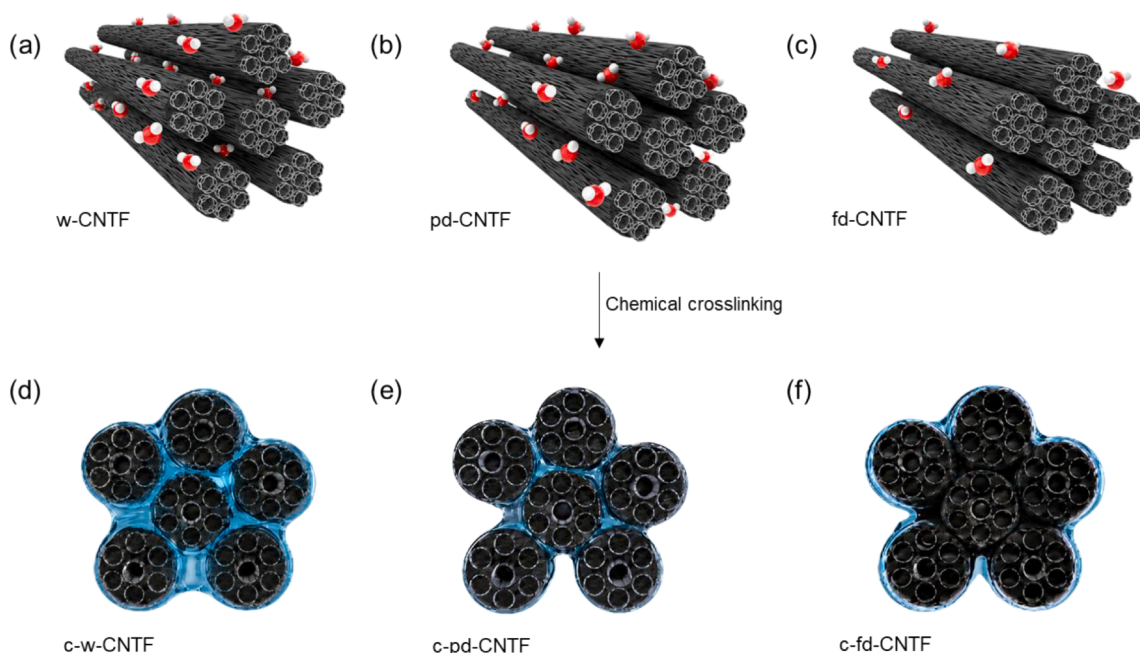


Fig. 1. Schematic illustration of drying-state-dependent bundle engineering and subsequent crosslinking in CNTFs. (a–c) Proposed bundle structures of (a) wet CNTF (w-CNTF), (b) partially dried CNTF (pd-CNTF), and (c) fully dried CNTF (fd-CNTF). (d–f) Proposed crosslink distributions obtained after crosslinking the corresponding precursor states: (d) c-w-CNTF, (e) c-pd-CNTF, and (f) c-fd-CNTF. (The schematic was prepared with the assistance of ChatGPT (OpenAI) using author-created CAD images.).

due to capillary effects. The evaporation of water induces capillary-driven densification, reducing the inter-bundle spacing and promoting the formation of more compact bundle assemblies, as illustrated in Fig. 1b. In the fully dried state (fd-CNTF), most of the interstitial and trapped water is removed, resulting in a highly consolidated and hydrophobic CNT network with severely restricted internal accessibility, as depicted in Fig. 1c.

These distinct drying states are expected to affect the infiltration behavior of aqueous chemical mediators during post-treatment. In w-CNTF, the abundant interstitial water allows the mediator to penetrate deeply into the fiber, leading to widespread functionalization

throughout the bundle network, as shown in Fig. 1d. In pd-CNTF, the residual water confined within inter-bundle regions can provide limited infiltration pathways, promoting preferential functionalization near bundle–bundle interfaces, as shown in Fig. 1e. In contrast, in fd-CNTF, the highly compact and hydrophobic structure strongly suppresses mediator penetration, causing functionalization to be largely restricted to the outer region of the fiber, as shown in Fig. 1f.

Fig. 2a–c presents the optical microscopy analysis of CNTF diameter variations according to drying conditions. In the case of w-CNTF stored in water, a significantly large diameter of 98 μm is observed, which is attributed to the substantial amount of water retained within the fiber

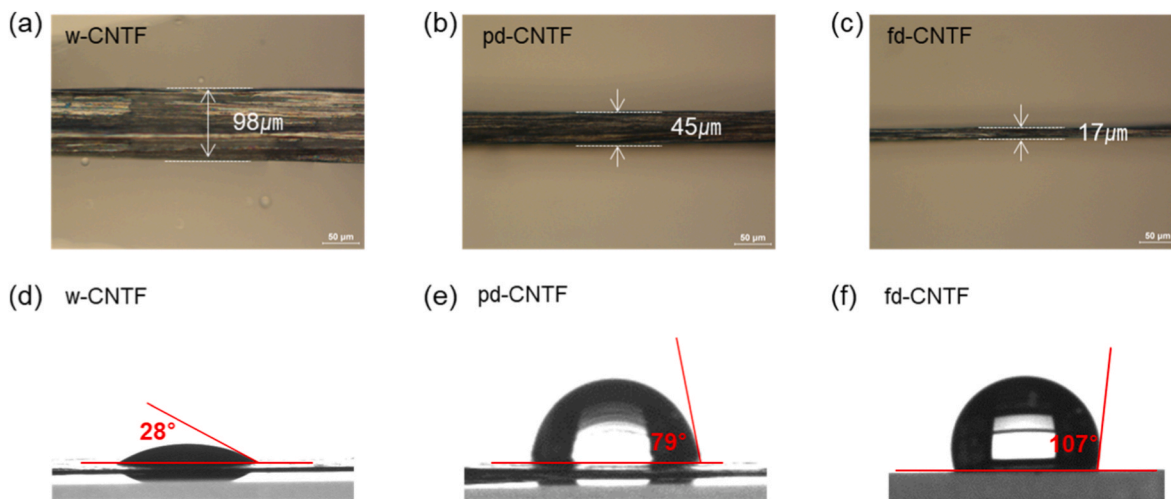


Fig. 2. Diameter and wetting behavior of CNTFs at different drying states. (a–c) Optical micrographs of (a) w-CNTF, (b) pd-CNTF, and (c) fd-CNTF, with the indicated fiber diameters. (d–f) Water contact-angle images of the corresponding fibers.

structure. However, the diameter decreases to 45 μm for pd-CNTF, and further reduces to 17 μm for fd-CNTF under more rigorous drying conditions. Fig. 2d–f shows the water contact angle (WCA) measurements used to evaluate the affinity between water and CNTFs dried under different conditions. Despite the intrinsic hydrophobicity of CNTs, w-CNTF exhibits a hydrophilic nature with a WCA of 28.0° , where water droplets spread rapidly upon contact due to the presence of water molecules within the bundles and on the surface. In contrast, the WCAs of pd-CNTF and fd-CNTF were measured at 79.0° and 107.0° , respectively. These results indicate that drying induces significant structural densification and restores the intrinsic hydrophobic nature of CNT surfaces, which is expected to influence the penetration of aqueous chemical mediators.

3.2. Drying-controlled accessibility of aqueous chemical mediator

The ECSA was measured to estimate the CNT surface area accessible to the aqueous chemical mediators, as ECSA represents a more practical metric for subsequent reactions than BET, which reflects the total physical surface area without considering electrolyte accessibility. As shown in Fig. 3a–c, the cyclic voltammetry (CV) curves of CNTFs were obtained in a non-faradaic potential window to determine the double-layer capacitance (C_{dl}). The rectangular shape of the CV curves and the linear increase in current with the scan rate indicate near-ideal capacitive behavior for all CNTFs. The actual ECSA measurements were evaluated by applying a specific capacitance of $17 \mu\text{F cm}^{-2}$ (see Supplementary material for details) [27]. The as-fabricated water-wetted CNTF exhibited an ECSA value of $35.2 \text{ m}^2 \text{ g}^{-1}$. This is significantly lower than the typical specific surface area of CNTFs measured by BET ($200 \text{ m}^2 \text{ g}^{-1}$) [28], representing the actual surface area of the CNTFs in contact with the aqueous solvent (Fig. 3d). As shown in Fig. 3e–f, the ECSA values of the pd-CNTF and fd-CNTF were $21.8 \text{ m}^2 \text{ g}^{-1}$ and $1.7 \text{ m}^2 \text{ g}^{-1}$, respectively, indicating that the surface area of the CNT bundle in contact with the aqueous chemical mediator decreases drastically as the degree of drying intensifies. This reduction is consistent not only with the residual moisture content shown in Fig. S3, but also with

the contact angle measurements, which can be attributed to the enhanced hydrophobicity induced by the more rigorous drying process. Furthermore, while rigorous drying promotes a highly densified structure through enhanced van der Waals interactions, the resulting loss of ECSA implies a significant reduction in the available sites for aqueous-based crosslinking agents. This leads to a structural bottleneck, where the densification of the internal bundle network hinders the uniform infiltration of functional groups required for both inter and intra-bundle covalent bonding.

3.3. Spatial control of functionalization and crosslinking

Fig. 4a and Fig. S4 present the XPS C 1s peak analyses performed to evaluate the surface chemical composition of CNTFs under different drying conditions. For quantitative comparison, the XPS components were categorized into C=C/C–C, C–O, C=O, and O=C–N/O=C–O groups, as the oxygen- and nitrogen-containing functionalities provide chemical evidence of the functionalization and subsequent crosslinking of the CNTFs. Prior to treatment, the fibers exhibited a high proportion of C=C and C–C bonds. Following post-treatment, the combined proportion of C=C and C–C bonds decreased from approximately 90% to 80%, accompanied by an increase in the relative proportions of C–O, C=O, and O=C–N/O=C–O groups. The characterization results obtained after the functionalization and crosslinking steps are shown in Fig. S5. The increased contribution of these functional groups after post-treatment therefore supports the successful chemical modification of the CNT fibers. Notably, their relative proportions remained comparable among the CNTFs regardless of the degree of drying. This trend was further corroborated by the Raman results shown in Fig. 4b and Fig. S6. While the I_G/I_D ratio of the pristine CNTF was measured to be 7.48, the crosslinked fibers (c-w-CNTF, c-pd-CNTF, and c-fd-CNTF) exhibited significantly lower but similar values of 2.67, 2.64, and 2.54, respectively, irrespective of the drying condition. These Raman results are consistent with the XPS analysis, indicating the partial transition of carbon atoms from sp^2 to sp^3 hybridization during the crosslinking process [29]. Furthermore, the polarized Raman results in Fig. 4c and

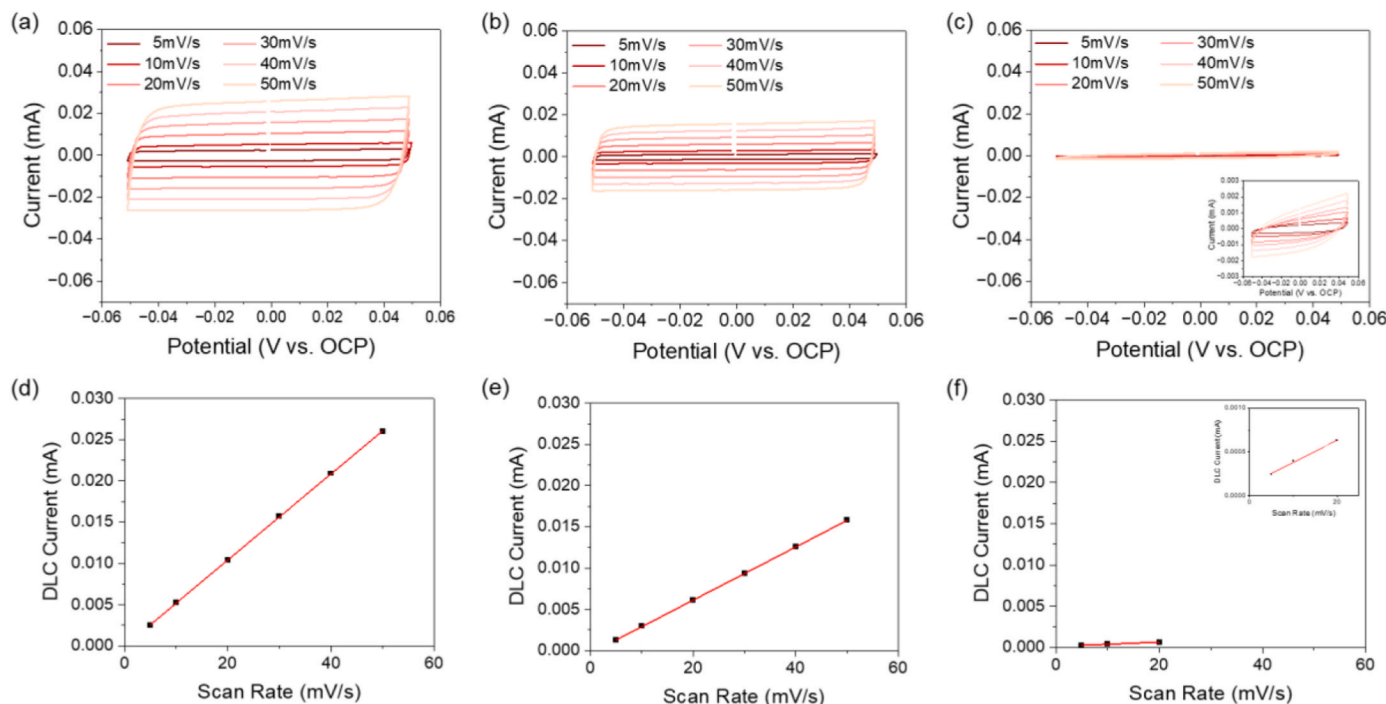


Fig. 3. Electrochemical evaluation of the accessible surface area of CNTFs under different drying conditions. (a–c) Cyclic voltammetry (CV) curves of CNTFs measured under different drying conditions. (d–f) Linear plots of double-layer capacitive current versus scan rate derived from the corresponding CV curves to determine the double-layer capacitance C_{dl} values.

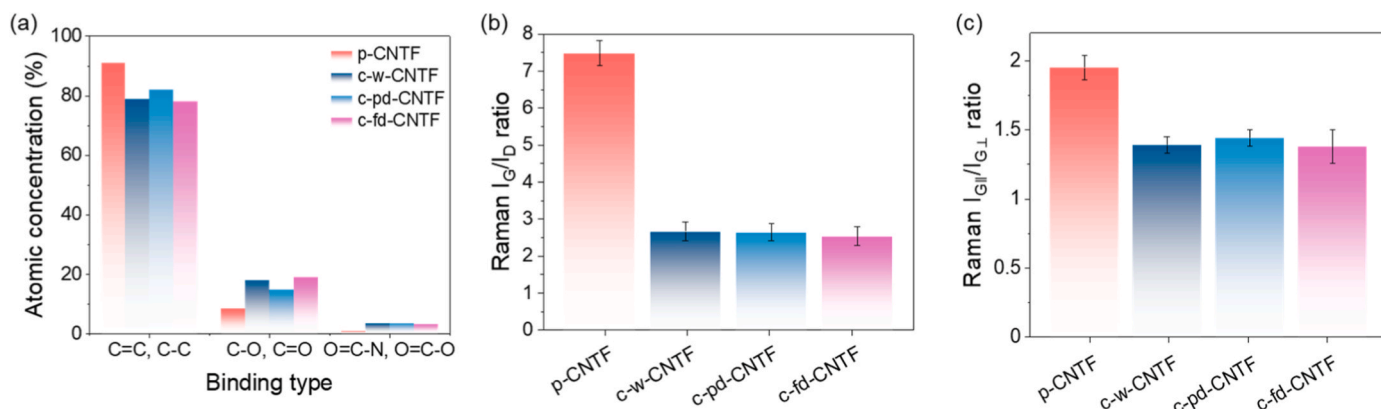


Fig. 4. Characterization of chemical composition and structural properties of CNTFs before and after crosslinking. (a) Atomic concentrations of carbon bonding types determined by XPS C 1s analysis. (b) Raman I_G/I_D ratios and (c) evaluation of CNTF alignment based on polarized Raman analysis.

Fig. S7 show that the $I_{G\parallel}/I_{G\perp}$ ratio was 1.95 for the p-CNTF, whereas it ranged from 1.38 to 1.44 for the crosslinked CNTFs. These small variations among the crosslinked samples may be associated with slight structural relaxation during solvent immersion and crosslinking, rather than differences in the drying conditions. Consequently, the drying condition does not significantly influence the overall orientation characteristics of the functionalized CNTFs. Taken together, these results indicate that drying primarily governs the spatial distribution of functionalization rather than the overall degree of functional group introduction or CNT alignment.

3.4. Load transfer efficiency

Fig. 5a–d presents the in situ Raman spectroscopy results used to evaluate the interfacial load transfer efficiency of CNTFs before and after crosslinking. The accompanying schematic illustrations in Fig. 5e–h provide mechanistic interpretations of the observed Raman behavior. It is well established that, when tensile stress is ideally transferred to individual CNTs without inter-bundle slippage, the G' peak shift can reach a slope of $37.5 \text{ cm}^{-1}/\%$ [30]. This value can therefore be used as an ideal reference for assessing stress transfer in macroscopic CNT assemblies. For p-CNTF, the G' peak shift rate was measured to be $14.4 \text{ cm}^{-1}/\%$, as shown in Fig. 5a, indicating inefficient stress transfer caused by interfacial slippage within the fiber structure.

After crosslinking, the CNTFs prepared under different drying states exhibited distinct stress transfer behaviors, as shown in Fig. 5b–d. In c-w-CNTF, the G' peak shift rate increased compared with p-CNTF,

indicating that the introduction of covalent bonds improves stress transfer to the constituent CNTs. However, because the abundant interstitial water allows the aqueous chemical mediator to penetrate broadly throughout the fiber, crosslinking is distributed over a wide region rather than being selectively concentrated at bundle–bundle interfaces. As schematically illustrated in Fig. 5f, extensive mediator infiltration produces broad functionalization, but the limited selectivity toward inter-bundle bonding likely restricts the improvement in macroscopic stress transfer in c-w-CNTF.

In contrast, c-pd-CNTF exhibited the highest G' peak shift rate of $25.2 \text{ cm}^{-1}/\%$, demonstrating the most efficient stress transfer among the crosslinked fibers. This improvement is attributed to the optimized partially dried state, in which free water is largely removed while a limited amount of residual water remains confined within inter-bundle regions. During this process, capillary-driven densification reduces the inter-bundle spacing and brings neighboring bundles into closer contact. At the same time, the remaining confined water may provide selective infiltration pathways for the aqueous chemical mediator. As a result, covalent bonding is expected to be preferentially formed at bundle–bundle interfaces, where stress transfer is most critical. The schematic in Fig. 5g illustrates that this inter-bundle crosslinking effectively suppresses bundle slippage and enables tensile stress to be more uniformly transferred across the hierarchical CNT bundle network.

For c-fd-CNTF, the G' peak shift rate was $17.7 \text{ cm}^{-1}/\%$, showing only a marginal improvement compared with p-CNTF. In the fully dried state, most interstitial and confined water is removed, resulting in a highly compact and hydrophobic CNT network [31]. This structure severely

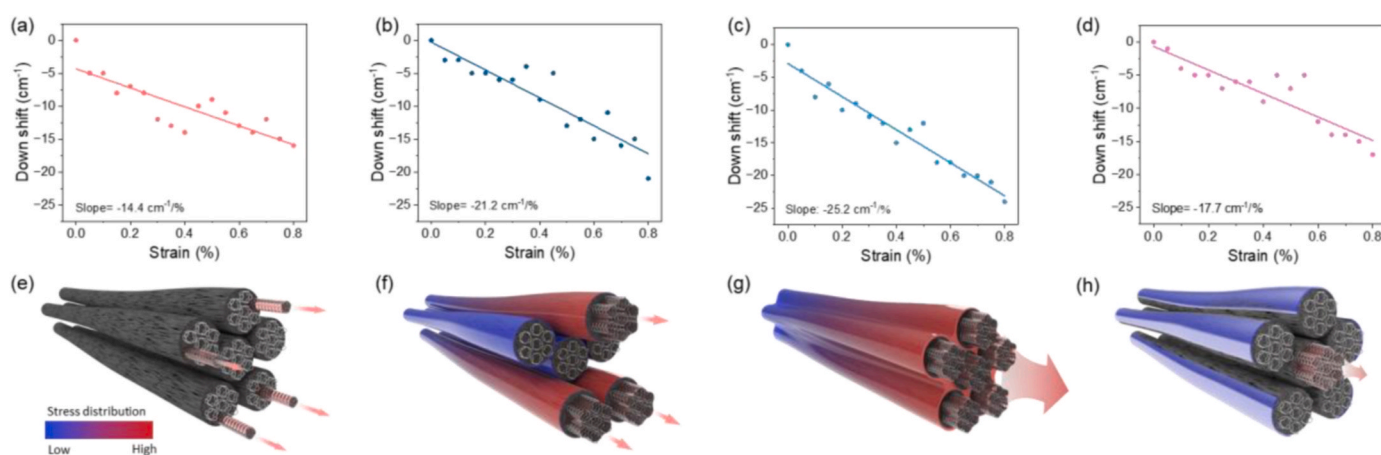


Fig. 5. In situ Raman analysis and schematic illustration of load transfer behavior in CNTFs. G' -band downshift rates under tensile loading and corresponding load transfer schematics for (a,e) p-CNTF, (b,f) c-w-CNTF, (c,g) c-pd-CNTF, and (d,h) c-fd-CNTF.

restricts the infiltration of the aqueous chemical mediator into the fiber interior. Consequently, crosslinking is expected to occur mainly near the outer region, as depicted in Fig. 5h. Although such surface-localized crosslinking can partially improve stress transfer near the fiber surface, the internal bundle interfaces remain insufficiently reinforced, limiting the overall load transfer efficiency.

These results and the cross-sectional analysis shown in Fig. S8 demonstrate that interfacial load transfer efficiency is not determined solely by the overall degree of functionalization but is governed by the spatial location of crosslinking within the hierarchical CNTF structure.

3.5. Mechanical properties and deformation behavior of CNTFs

Fig. 6, Table 1 and Table S1 present the tensile test results of the pristine p-CNTF and the crosslinked CNTFs prepared under different drying conditions. The p-CNTF exhibited a specific strength of 1.69 N tex^{-1} and a specific stiffness of 129.9 N tex^{-1} . Due to the absence of covalent bonding between the bundles, the applied load was largely accommodated by inter-bundle slippage, resulting in a strain at break of approximately 4%. In contrast, the crosslinked fibers (c-w-CNTF, c-pd-CNTF, c-fd-CNTF) showed a reduction in ductility regardless of the drying condition, with strain-at-break values ranging from 2.21% to 2.82%. This reduction in strain suggests that chemical crosslinking suppresses inter-bundle slippage and promotes a more rigid load-bearing network.

Interestingly, the reinforcement efficiency varied significantly depending on the drying state prior to crosslinking. As illustrated in Fig. 1d–f, c-w-CNTF is expected to involve broadly distributed or intra-bundle-dominant crosslinking, whereas c-fd-CNTF is expected to involve surface-localized crosslinking. Specifically, c-w-CNTF exhibited a

specific strength of 2.36 N tex^{-1} and a specific stiffness of 171.1 N tex^{-1} , whereas c-fd-CNTF exhibited a specific strength of 1.85 N tex^{-1} and a specific stiffness of 169.9 N tex^{-1} . However, the highest reinforcement efficiency was observed in c-pd-CNTF, which is supported by Fig. S9, indicating that crosslinking does not induce internal densification of the fiber but is instead expected to be preferentially formed at bundle–bundle interfaces. This sample achieved a superior specific strength of 2.47 N tex^{-1} and a specific stiffness of 207.6 N tex^{-1} , demonstrating superior mechanical properties compared to previously reported crosslinked CNTFs (Fig. 6c) [22,24,25,29,32–35]. This trend is consistent with the load transfer efficiency confirmed by in situ Raman spectroscopy and is further supported by the fracture morphology shown in Fig. 6d.

The tensile fracture surfaces of p-CNTF and crosslinked CNTFs exhibit contrasting failure modes. In p-CNTF, the interfaces between CNT bundles are predominantly governed by weak van der Waals interactions. Under tensile loading, this weak inter-bundle coupling allows progressive bundle sliding and pull-out, resulting in a tapered fracture morphology with extended pulled-out bundles. In contrast, the crosslinked fibers demonstrate a more uniform fracture pattern with relatively shorter pull-out bundle lengths compared to p-CNTF, indicating more effective stress transfer throughout the network [36]. Furthermore, the effectiveness of crosslinking is reflected in the distinct differences in the diameters of the pulled-out bundles among the crosslinked samples. In the case of c-fd-CNTF, which exhibited the smallest bundle size after extraction, the specific stiffness increased compared to that of p-CNTF due to surface-localized crosslinking. However, the improvement in specific strength was limited, suggesting that surface-localized crosslinking does not effectively redistribute stress throughout the internal bundle network and may leave internal

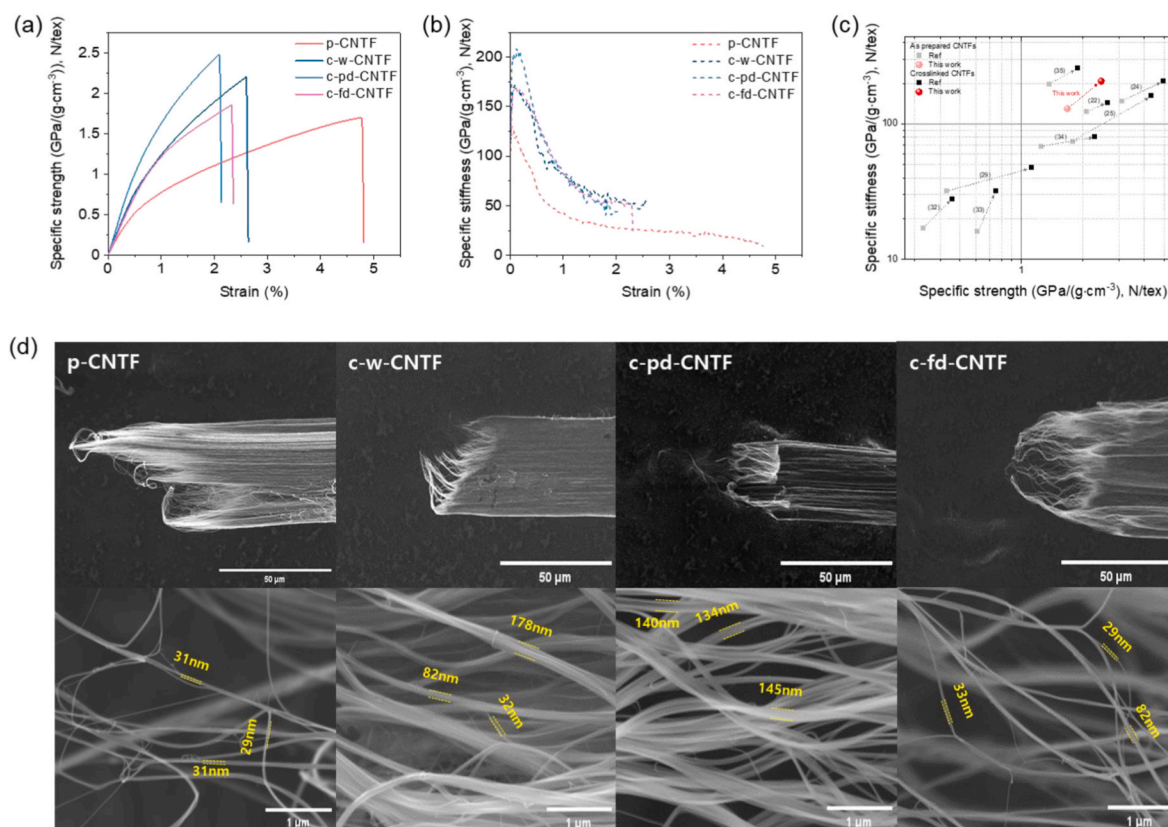


Fig. 6. Mechanical properties and fracture morphology investigations of CNTFs under different drying conditions. (a) Specific strength-strain curve and (b) corresponding specific stiffness-strain profiles of pristine and crosslinked CNTFs under various drying states. (c) Comparison of the specific stiffness and specific strength between previously reported crosslinked CNTFs and c-pd-CNTF. (d) Low- and high-magnification SEM images showing the fracture surfaces and internal bundle structures of the respective CNTFs after tensile failure.

Table 1

Comparison of the mechanical properties of p-CNTF and crosslinked CNTFs prepared via different drying conditions. (The specimen number (n) is indicated for each fiber).

	Tex (g km ⁻¹)	Specific strength (GPa/(g cm ⁻³))	Specific stiffness (GPa/(g cm ⁻³))	Strain (%)	Toughness (J g ⁻¹)
p-CNTF (10)	0.14 ± 0.06	1.69 ± 0.15	129.9 ± 16.0	3.92 ± 0.31	44.3 ± 7.4
c-w-CNTF (9)	0.27 ± 0.08	2.36 ± 0.56	171.1 ± 38.4	2.82 ± 0.46	46.4 ± 16.1
c-pd-CNTF (9)	0.25 ± 0.04	2.47 ± 0.49	207.6 ± 37.1	2.57 ± 0.45	51.3 ± 14.1
c-fd-CNTF (10)	0.23 ± 0.02	1.85 ± 0.22	169.9 ± 19.3	2.21 ± 0.39	27.1 ± 7.5

interfaces susceptible to sliding. In contrast, c-pd-CNTF exhibited a fracture morphology favorable for mechanical reinforcement, with uniformly formed large bundles exceeding 130 nm in diameter. The larger pulled-out bundle diameter suggests that neighboring bundles were mechanically coupled by inter-bundle crosslinks and fractured as integrated load-bearing units, contributing to the enhanced stiffness and strength of c-pd-CNTF. These results indicate that mechanically effective crosslinking depends not only on the presence of covalent junctions but also on their spatial placement within the drying-dependent bundle structure.

Having confirmed the enhanced tensile properties of c-pd-CNTF, we further evaluated whether this optimized interfacial structure could maintain mechanical stability under solvent exposure and complex deformation conditions. Fig. 7 presents the deformation behavior and mechanical stability of CNTFs after post-treatment under solvent exposure and complex deformation conditions. To examine the solvent-

induced deformation behavior, water and isopropyl alcohol (IPA) droplets were brought into contact with the fibers at approximately 1% strain during tensile testing. In addition, knot tensile tests were performed by measuring the mechanical strength of knotted fibers, and dynamic work recovery was evaluated through cyclic loading-unloading tests.

Because p-CNTF has an intrinsically hydrophobic surface, water infiltration into the fiber interior is limited, resulting in negligible changes in tensile strength after water exposure. In contrast, the crosslinked CNTFs became more hydrophilic after chemical functionalization, as shown in Fig. S10, which could promote water infiltration and induce solvent-assisted inter-bundle slippage. Nevertheless, the cross-linked fibers maintained their mechanical strength even after water exposure, indicating that covalent crosslinking effectively stabilizes the CNT bundle network against water-induced slippage.

A more pronounced solvent effect was observed under IPA exposure,

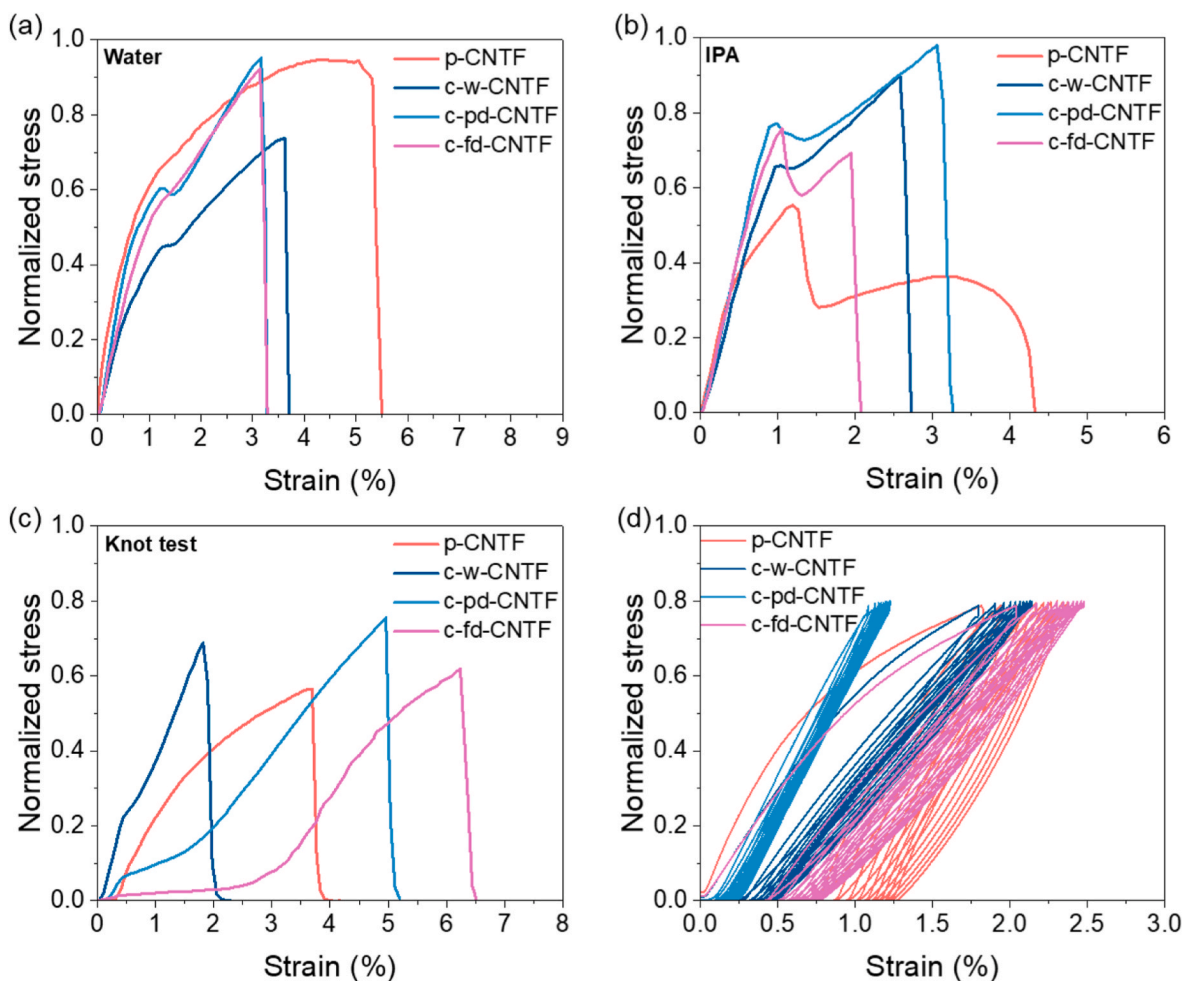


Fig. 7. Mechanical stability and solvent-induced response of pristine and crosslinked CNTFs under various environmental and loading conditions. Normalized stress-strain curves of the CNTFs exposed to (a) water and (b) IPA at a tensile strain of 1%. (c) Normalized stress-strain profiles obtained from knot tests and (d) cyclic loading-unloading curves demonstrating the energy dissipation behaviors of the CNTFs.

as shown in Fig. 7b. Unlike water, IPA more readily infiltrated the p-CNTF network and induced bundle swelling and lubrication, thereby significantly reducing mechanical strength [37]. In contrast, the crosslinked fibers retained their strength, indicating that covalent bonds effectively inhibited solvent-induced bundle swelling and slippage. Among them, c-pd-CNTF showed the highest strength retention, which can be attributed to preferential inter-bundle crosslinking at the most effective load-transfer interfaces.

The superior deformation stability of c-pd-CNTF was further supported by the knot test and dynamic work recovery (DWR) test shown in Fig. 7c–d. The knot test indicates that c-pd-CNTF maintains structural integrity under severe bending and localized stress concentration. The DWR test confirms a more reversible deformation and reduced irreversible energy dissipation under cyclic loading [38]. Fig. S11 shows the DWR calculated from the first loading–unloading cycle, enabling comparison without the accumulation of permanent deformation. While p-CNTF, c-w-CNTF, and c-fd-CNTF exhibited DWR values of 47.6%, 65.2%, and 56.9%, respectively, c-pd-CNTF showed the highest dynamic work recovery, with a DWR of 91.8%.

The DWR behavior under cyclic loading highlights that load-bearing pathways and mechanical reversibility are highly sensitive to the spatial distribution of crosslinks, rather than only to the total degree of functionalization [38–40]. When crosslinking is mainly restricted to the outer region of the fiber, as expected in c-fd-CNTF, the internal bundles are likely to remain insufficiently reinforced and rely primarily on weak van der Waals interactions and inter-bundle friction [41]. Under cyclic deformation, this structural heterogeneity may induce modulus mismatch and localized stress concentration near the boundary between crosslinked and insufficiently reinforced regions, leading to irreversible interfacial sliding and macroscopic energy dissipation [42]. These results demonstrate that the partially dried state enables the most effective interfacial crosslinking architecture, leading not only to enhanced tensile performance but also to improved mechanical reliability under solvent exposure and complex deformation conditions.

4. Conclusion

In this study, we systematically investigated the role of drying in governing the structural evolution, chemical accessibility, and mechanical performance of CNTFs. Progressive drying induced capillary-driven densification of the CNT bundle network, leading to enlarged bundle structures and increased hydrophobicity, as evidenced by the increase in water contact angle. At the same time, ECSA analysis revealed that excessive drying significantly reduced the surface area accessible to aqueous chemical mediators, thereby limiting reagent penetration into the internal fiber structure.

Among the different drying states, the partially dried condition provided the most effective balance between structural densification and chemical accessibility. In wet CNTFs, extensive mediator infiltration resulted in broadly distributed functionalization, whereas fully dried CNTFs restricted mediator access mainly to the outer fiber region because of severe densification and hydrophobic recovery. In contrast, partially dried CNTFs allowed the crosslinking reagent to access mechanically vulnerable bundle–bundle interfaces, enabling more effective inter-bundle covalent crosslinking.

This optimized crosslinking configuration significantly improved interfacial load transfer efficiency, as demonstrated by the highest Raman G'-band shift rate under tensile strain, and led to superior mechanical performance. The partially dried and crosslinked CNTFs (c-pd-CNTF) exhibited the highest specific strength and stiffness, along with enhanced mechanical reliability under cyclic loading, knot deformation, and solvent exposure. These findings highlight that drying is not merely a passive processing step but a critical structural design parameter that dictates the balance between CNT bundle densification and chemical accessibility. The present work provides a comprehensive understanding of the interplay between drying-induced structural evolution and

crosslinking efficiency, offering a practical strategy for designing high-performance CNTFs through controlled wet-state engineering.

CRediT authorship contribution statement

Jinho Jang: Writing – original draft, Methodology, Investigation. **Kyung Tae Park:** Investigation, Conceptualization. **Kyunbae Lee:** Investigation. **Minseouk Choi:** Investigation. **Dong Uk Woo:** Investigation. **Changsoon Choi:** Supervision, Conceptualization. **Taecheon Kim:** Supervision, Project administration, Funding acquisition. **Yeonsu Jung:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the authors used ChatGPT (OpenAI) in order to enhance the aesthetic quality and visual clarity of the author-created CAD images. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. ASupplementary data

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