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Supplementary

Enhancing the Interfacial Shear Strength and Tensile Strength of Carbon Fibers through Chemical Grafting of Chitosan and Carbon Nanotubes

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EDS analysis of CF@CS surface elements:

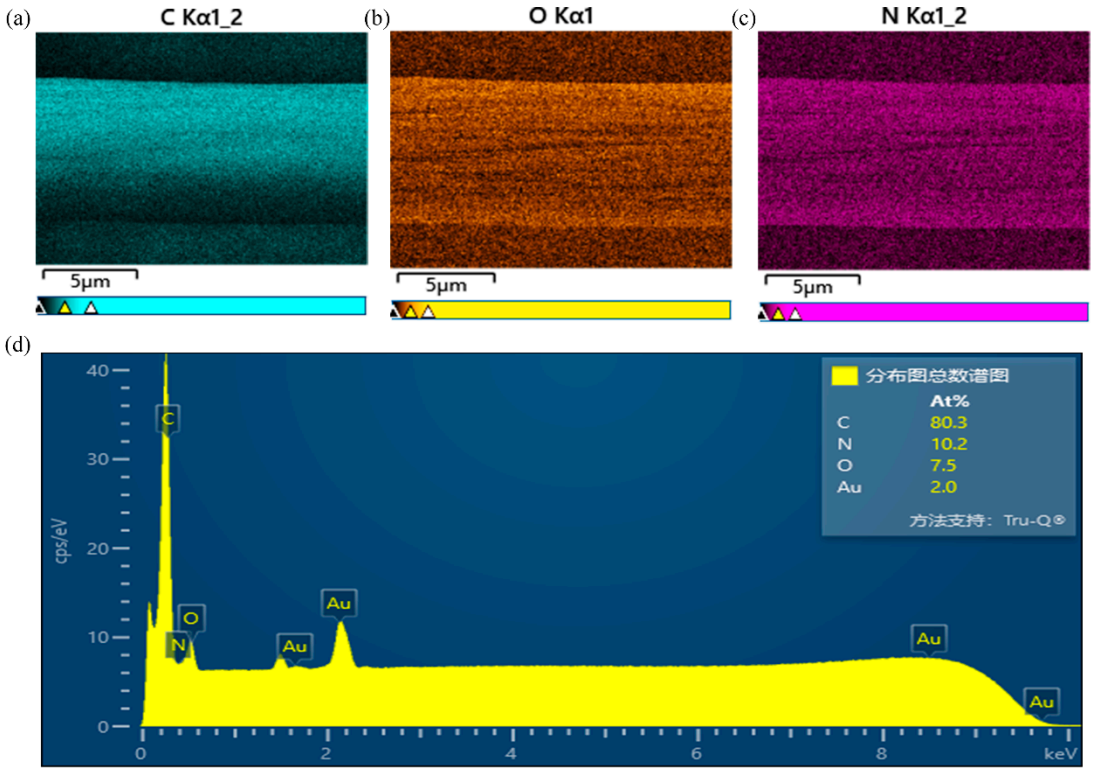

Figure S1. EDS diagrams of CF@CS: (a) distribution image of C, (b) distribution image of O, (c) distribution image of N, (d) total spectrum of distribution image.

Large magnification TEM image of the CNT layer in CF@CS@CNT2： The CNTs were clustered together on the surface of CF, forming a "network-like" structure with no obvious orientation.

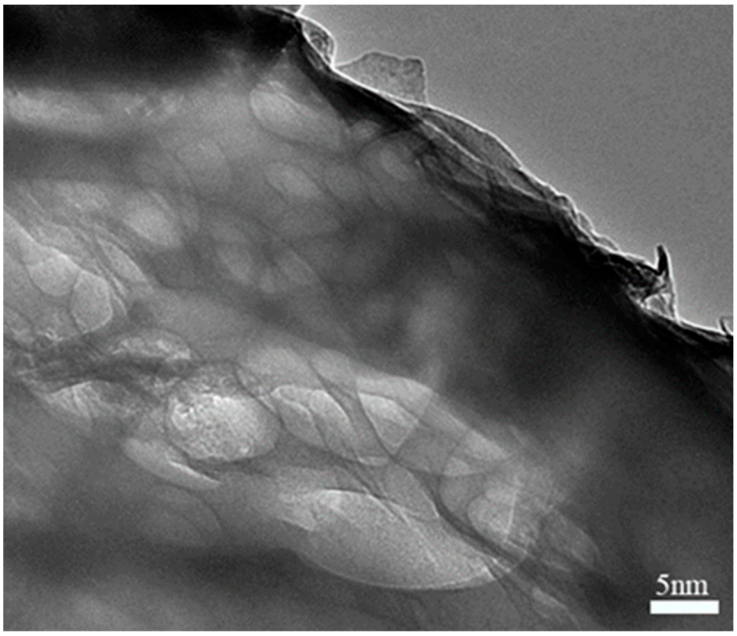

Figure S2. Large magnification TEM image of the CNT layer in CF@CS@CNT2.

SEM images of different contents of CNTs: (a) CF@CS@CNT1 for 0.025wt.% of CNTs (b) CF@CS@CNT1 for 0.05wt.% of CNTs (c) CF@CS@CNT1 for 0.1wt.% of CNTs (d) CF@CS@CNT1 for 0.15wt.% of CNTs

The morphological changes were observed when the samples were grafted with different concentrations of CNTs, as the CFs surface roughness increased significantly. When the CNTs concentration was 0.025 wt.% since the amino group of CS could react chemically with the carboxyl groups of different parts of the CNTs, resulting in an inverted distribution of CNTs on the surface of CF (Fig. S2a). However, due to the low CNTs concentration, the CNTs were randomly dotted and unevenly distributed on the CFs surface. When the CNT concentration increased further, the CNTs were more and more densely distributed on the CFs surface, and the distance between the tube bundles decreased, resulting in a uniform CNTs network layer (Fig. S2b). When the CNTs concentration was 0.1 wt.%, due to the strong van der Waals forces of the CNTs, the densely grafted CNTs showed little agglomeration on the CFs surface (Fig. S2c). Upon increasing the CNTs concentration to 0.15 wt.%, the bundles of CNTs became closer together and more obvious agglomeration occurred (Fig. S2d).

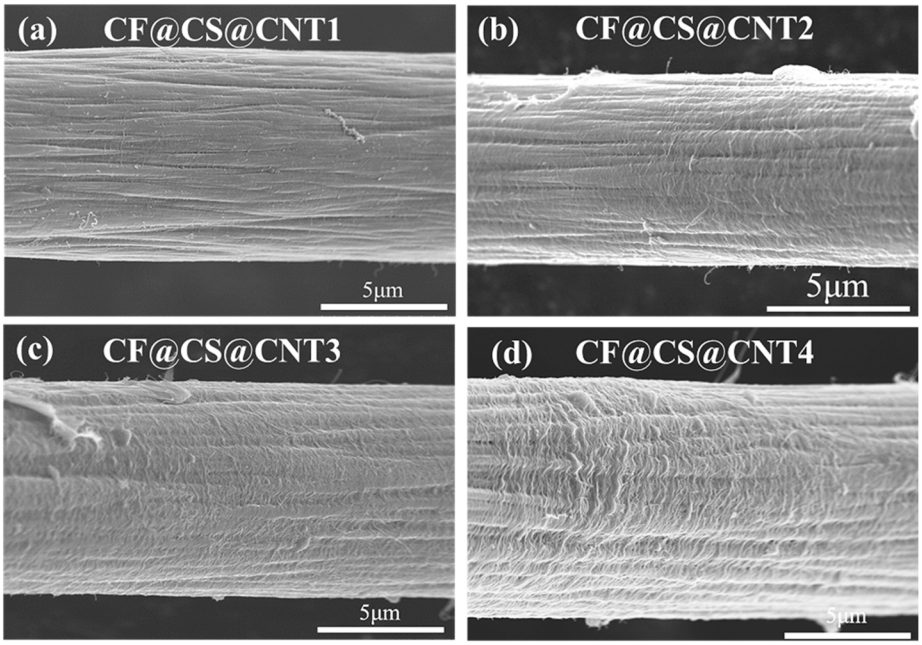

Figure S3. SEM images: (a) CF@CS@CNT1, (b) CF@CS@CNT2, (c) CF@CS@CNT3, (d) CF@CS@CNT4.

Raman images of different samples:

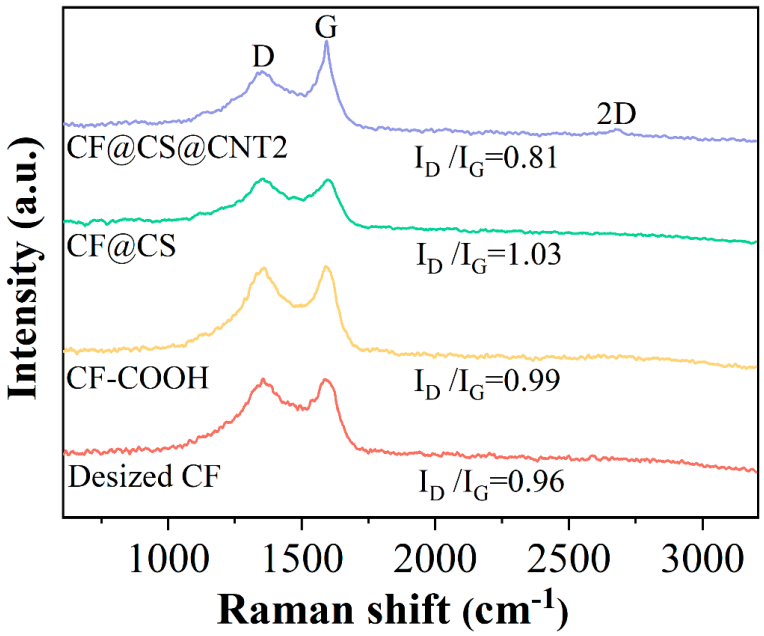

Figure S4. Raman images of different samples.

Specific data for each sample IFSS:

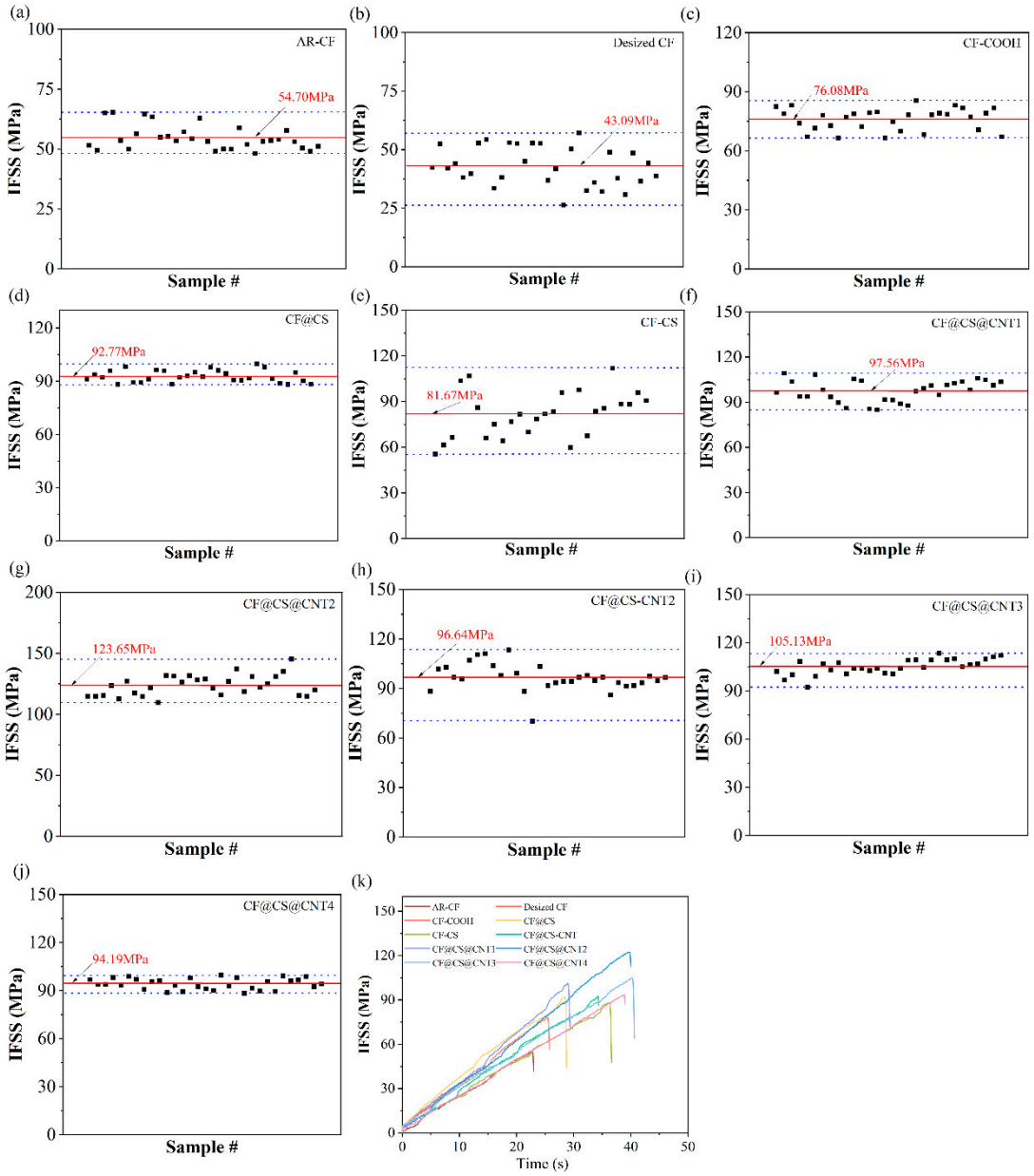

Figure S5. IFSS specific data: (a) AR-CF, (b) desized CF, (c) CF-COOH, (d) CF@CS, (e) CF-CS, (f) CF@CS@CNT1, (g) CF@CS@CNT2, (h) CF@CS-CNT2, (i) CF@CS@CNT3, (j) CF@CS@CNT4, (k) The typical stress-strain curves for IFSS.

Comparison of IFSS performance with other literature and references:

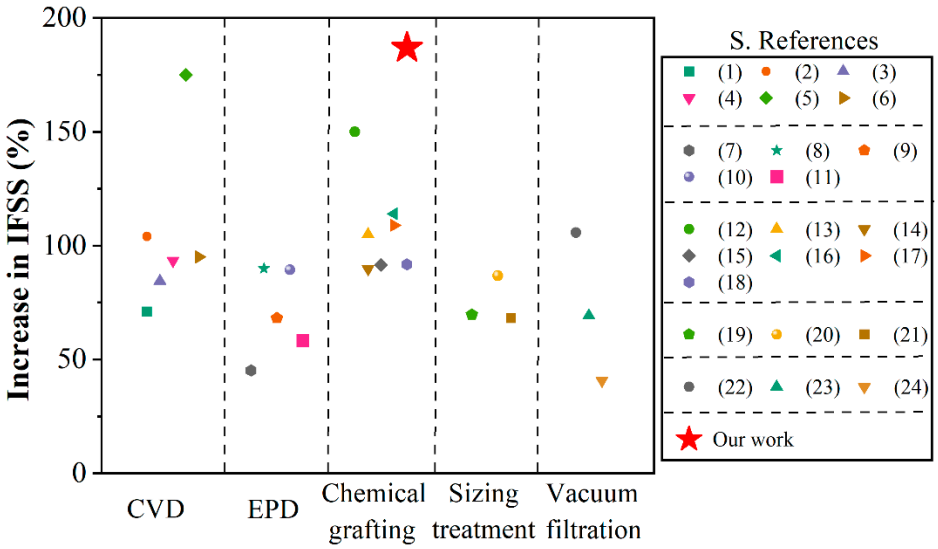

Figure S6. IFSS performance comparison.

Summary table of the performance of the samples with different CNT concentrations:

Table S1. Comparison of the performance of different samples.

Sample	CNT concentrations (wt.%)	IFSS (MPa)	Tensile strength (GPa)
CF@CS@CNT1	0.025	97.56	5.87 (±0.94)
CF@CS@CNT2	0.05	123.65	6.01 (±0.74)
CF@CS@CNT3	0.1	105.13	6.04 (±0.87)
CF@CS@CNT4	0.15	94.19	6.11 (±0.81)

As CNTs concentrations increased, the tensile properties of CF@CS@CNT improved slightly, as shown in Tab. S1. In this work, various CNTs concentrations were used to investigate the effect of CNTs on IFSS properties, and the monofilament tensile test was only used to prove that the method we proposed was not detrimental to the mechanical properties of the fibers. Therefore, in this work, we chose IFSS performance as the main consideration factor to determine the effect of CF surface modification, and CF@CS@CNT2, which showed the highest IFSS performance, was selected to be detailed studied. For CF@CS@CNT2, this apparent increase can be attributed to three aspects: (1) The increase of CNT concentration will increase the surface roughness of CFs and enhance the mechanical locking between fiber and resin. (2) The functionalized CNTs can react chemically with the resin to enhance the strength of the epoxy resin at the interface; the connection between CF and CS, CS and CNTs all rely on strong covalent bonds, and the CNTs can not be peeled off easily from the interface when subjected to shear forces. Therefore, a higher force is needed to pull CNTs out of the resin. (3) The cracks propagating in the resin will be deflected away from the CFs surface when they encounter CNTs.

However, the IFSS of CF@CS@CNT3 decreased slightly from 123.65 MPa to 105.13 MPa due to the "over-covering" of CNTs. On the one hand, too much CNTs would increase the thickness of the interfacial layer, which is not conducive to stress transfer; on the other hand, in the over-thick CNTs layer, only some of the CNTs in close contact with CS could form strong covalent bonds, while the rest of CNTs can only interact with each other through van der Waals interaction. Due to the weak van der Waals interaction between CNTs, interfacial defects may appear inside the CNTs, leading to a decrease in

IFSS values. In addition, narrow gaps between CNTs can restrict the flow of resin to the CF's surface, resulting in poor interfacial adhesion between CFs and epoxy resin[25,26].

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