

Supplementary Information: Carbon Nanotube Survivability in Marine Environments and Method for Biofouling Removal

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I. CNT Corrosion Stability

A corrosion study was conducted to evaluate CNT material stability in ASTM D1141 simulated seawater over a time greater than the deployment period. Figure S1a shows the as-received CNT sheet material immediately after submersion in 20 mL of stagnant simulated seawater. The sample was exposed at 21°C under static conditions with regular monitoring to assess physical changes, and Figure S1b shows the results after more than 12 months. The as-received CNTs and corresponding saltwater solution, remain physically unchanged by visual inspection for the entire observation period. While the corrosion susceptibility of traditional metals, like copper and steel, is well documented,(Farro et al. 2009) (Alcantara et al. 2017) the robust nature of the CNTs in static simulated seawater suggests that CNTs may be an attractive material for marine applications. These results, combined with recently published work showing the superior Tafel corrosion potential of CNTs compared to Cu,(Tomkiewicz et al. 2020) demonstrate the inherent saltwater stability of CNTs, which warrants additional investigation in a realistic marine environment.

As-Received CNT Ribbon

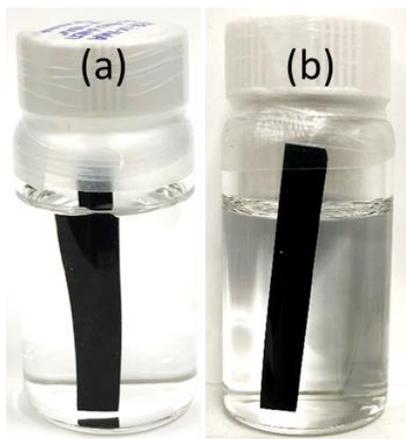


Figure S1. Representative photographs showing the corrosion susceptibility of a bulk as-received carbon nanotube ribbon. The photograph in (a) shows the sample immediately after submersion (control), and (b) shows the state of the sample after 14 months of exposure in static simulated seawater at 21°C.

II. Thermogravimetric Analysis of Marine Deployed CNTs As A Function of Time

Thermogravimetric analysis (TGA) was performed on a portion of each biofouled CNT coupon following marine exposure and recovery. Figure S2a and Figure S2b show the representative thermogram and first derivative weight loss data, respectively, for the as-received CNT samples before (black curve) and after (red curves) deployment. The data corresponding to the as-received CNT control sample (no ocean exposure) shows a broad decomposition feature between 100°C - 400°C, which is attributed to desorption of adsorbed water and decomposition of carbonaceous impurities. The onset of CNT decomposition occurs at approximately 425°C, with a maximum rate of CNT decomposition observed at approximately 625°C. There is ~19% residual mass observed, which is composed of the iron catalyst remaining from the CNT synthesis process. An additional low temperature decomposition feature is observed at ~300°C for the CNT samples deployed for 4 and 8 months, which is attributed to the decomposition of organic matter from soft biofouling agents (*i.e.*, slime). A shift in the maximum CNT decomposition from ~625°C to $\geq 665^\circ\text{C}$ is observed after biofouling. This may be the result of the sample being starved for oxygen until enough of the biogrowth is removed from the surface of the sample to allow for oxidation. An increase in residual mass to ~35% is observed for the 4-month exposed sample, and ~49% for the 8-month exposed sample. This demonstrates that the extent of biofouling, as well as sand and salt infiltration, increases with exposure time. The inset photograph in Figure S2a shows the TGA test sample before and after experiencing a temperature of 1000°C in air. The presence of silicon dioxide and calcium carbonate in the form of hard biofoulers and sand, as well as the various salts deposited in the CNT network, are expected to contribute significantly to the increased residual mass.

By comparison, Figure S2c and Figure S2d show the thermogram and first derivative weight loss for the cyanoacrylate-treated CNT coupons before (grey curve) and after (red curves)

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deployment. Figure S2c shows that the cyanoacrylate-treated samples exhibit significant decomposition below 400°C. Analysis of the first derivative data in Figure S2d shows that this mass loss is attributed to the oxidation of the surface treatment, which is confirmed by comparison of neat cyanoacrylate, as shown in the figure inset. Additionally, the cyanoacrylate-treated CNTs exhibit a reduced residual mass of ~4%. Although this is less than the 19% residual mass measured for the as-received CNT control, it is important to note that the cyanoacrylate accounts for 80% of the sample mass, and the ratio of CNTs to iron oxide is nominally equivalent between the cyanoacrylate-treated and as-received samples (3.0 vs 3.5, respectively). After deployment, there is an increase in residual mass for all recovered samples, which is consistent with the as-received samples. The increase in residual mass ranges from ~8 – 22%, however, the increase is not monotonic with exposure time (*i.e.*, biofouling increases 8 < 4 < 12 months). The inconsistency in residual mass with exposure time is related to: (1) the nonuniform coverage of biofouling across the CNT samples causing the residual mass to be variable over the entire sheet, and (2) the biofouling does not adhere strongly to the cyanoacrylate-treated CNTs, allowing the biofouling to easily delaminate while removing a section of the sample for analysis.

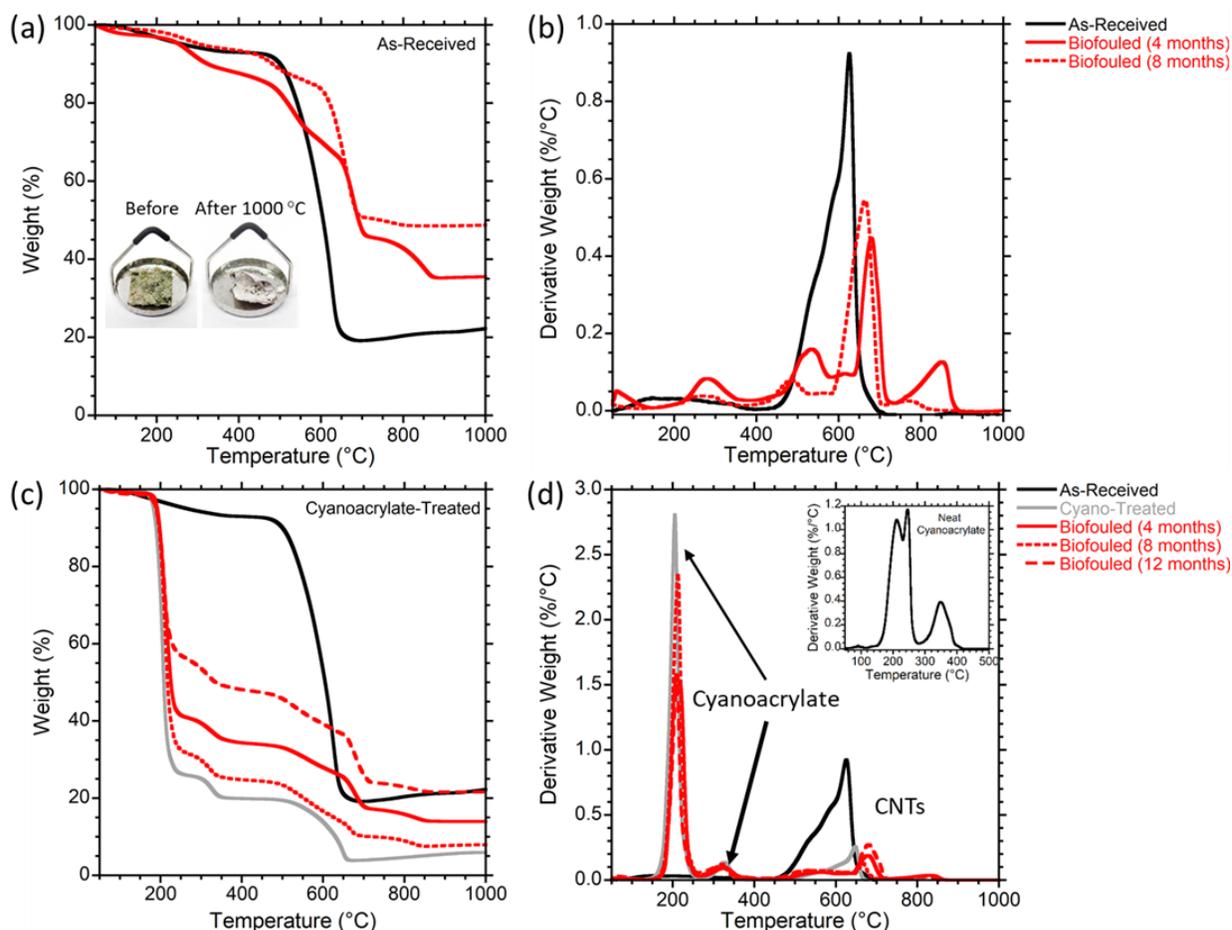


Figure S2. Thermogravimetric analysis of the (a) percent weight and (b) first derivative weight loss for as-received CNTs before (black curve) and after (red curves) ocean deployment as a function of exposure time. The inset in (a) shows a representative photograph of the biofouled sample exposed for 8 months before analysis compared to the residue remaining after exposure to 1000°C in air. (c) and (d) show the thermogram and first derivative weight loss for the cyanoacrylate-treated CNTs before (grey curve) and after (red curves) marine deployment as a function of exposure time. The inset in (d) shows the first derivative weight loss of neat cyanoacrylate as a control.

III. Biofouling Adhesion on CNTs

Figure S4 demonstrates the difference in biofouling adhesion between the as-received and cyanoacrylate-treated CNTs. The leftmost photograph in each pair shows the CNT ribbons (approximately 0.5 cm × 4 cm (W×L)) that were cut from the samples deployed in the ocean for

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8 months. For comparison the rightmost photographs in each pair show the same ribbon samples after being rolled, manipulated, and gently scraped several times. This qualitative analysis demonstrates that the biogrowth is strongly adhered to the as-received CNT sample, whereas Figure S4b displays the poor adhesion of the biofouling on the cyanoacrylate-treated CNTs.

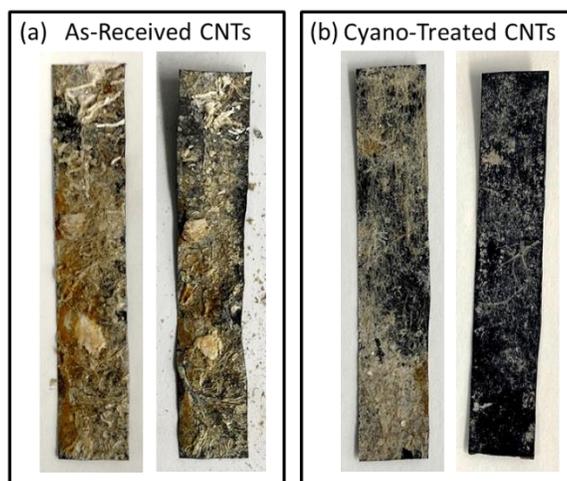


Figure S3. Representative photographs highlighting the difference in biofouling adhesion between the (a) as-received and (b) cyanoacrylate-treated CNT samples. The leftmost photograph in each pair shows a ribbon cut from the respective coupon after 8 months of ocean exposure, and the rightmost photograph shows the same ribbon after manual manipulation.

IV. Thermogravimetric Analysis of HCl-Treated CNTs After Marine Deployment

A post-exposure purification technique was proposed for the removal of biofouling from the CNT coupons after ocean exposure. The samples were soaked in HCl for 10 min, followed by thermal oxidation to 500°C. This process was repeated twice to ensure complete removal of the biogrowth. Thermogravimetric analysis (TGA) was used to quantify the efficacy of the proposed purification technique, and the weight loss data is provided in Figure 4 of the main text. Analysis of the first derivative weight loss in Figure S4a shows an increase in the maximum CNT decomposition temperature from 625°C for the as-received control to >650°C after biofouling and HCl treatment, suggesting that there is an increase in CNT purity after treatment. The same trend

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in CNT decomposition temperature is observed for the cyanoacrylate-treated CNTs shown in Figure S5b. It is also evident from this data that the cyanoacrylate surface coating remains intact through the post-exposure purification, thus validating this approach for removing biofouling from both the as-received and cyanoacrylate-treated CNTs.

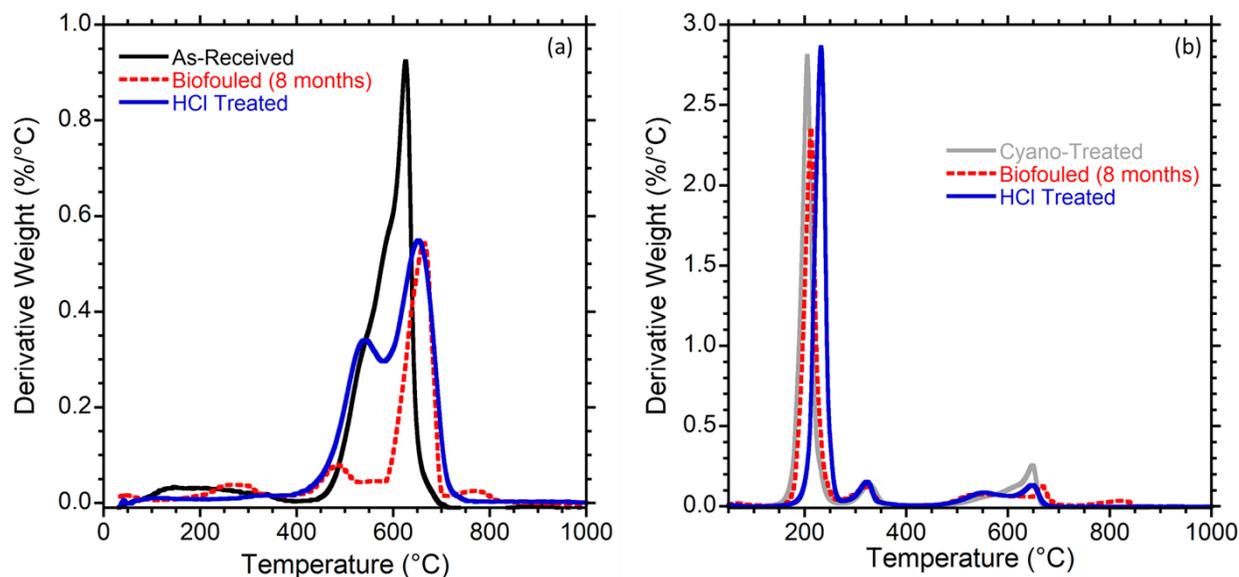


Figure S4. Thermogravimetric analysis of the first derivative weight loss for (a) as-received and (b) cyanoacrylate-treated CNT sheet material as a function of temperature. The red curves show the effect of biofouling after an 8-month ocean deployment, and the blue curves show the impact of the post-recovery HCl treatment.

V. HNO₃ Treatment of Biofouled CNTs

Post-exposure purification of the CNTs was performed using HNO₃, and the results were compared to those obtained for HCl. Figure S5a and Figure S5b show the TGA weight loss and first derivative weight loss of the as-received CNTs, respectively. Figure S5a shows that the HNO₃ treatment after biofouling effectively reduces the residual mass back to the baseline, indicating complete removal of the biogrowth. Unlike the HCl treatment, the HNO₃ treatment does not cause an improvement in CNT purity, and the residual iron catalyst and carbonaceous

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impurities present from synthesis remain unchanged when compared to the as-received sample. However, it can be concluded that both HCl and HNO₃ treatments are effective at removing biofouling from the CNTs, and thus, characterization of the physical and electrical properties of the acid-treated CNTs is required.

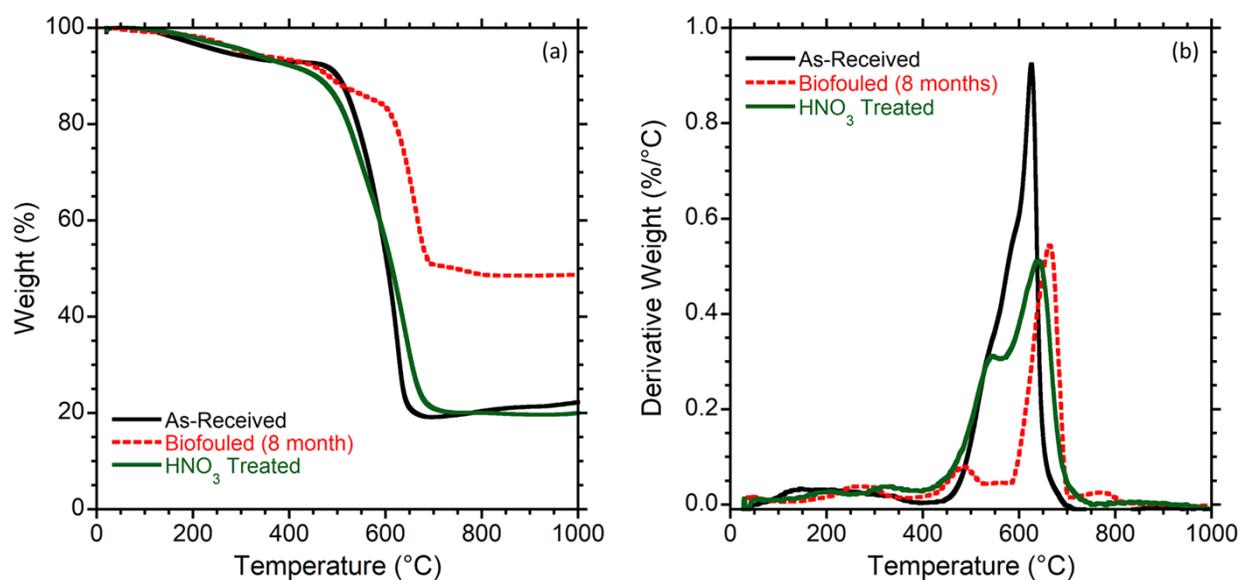


Figure S5. Thermogravimetric analysis of the (a) weight loss and (b) first derivative weight loss for the as-received CNT sheet material showing the effect of biofouling (8-month ocean deployment) and subsequent HNO₃ treatment.

The as-received CNT material has a measured R/L of 123 Ω /m. After 8 months of ocean deployment, and subsequent HNO₃ treatment and thermal oxidation, the R/L decreases to 100 Ω /m, which represents a 19% decrease. These samples were subsequently subjected to current carrying capacity (CCC) testing, in which the voltage was ramped at a constant rate and the maximum current at failure monitored. Figure S6 shows the current-voltage profile of an as-received control sample (no ocean exposure) compared to a sample deployed in the ocean for 8 months and subsequently HNO₃-treated. The HNO₃-treated CNT sample exhibits a maximum current at failure of 1.53 A, compared to 1.69 A for the as-received control. Although this is a

decrease in CCC, these results are expected based on the decrease in R/L measured for this sample after acid treatment.

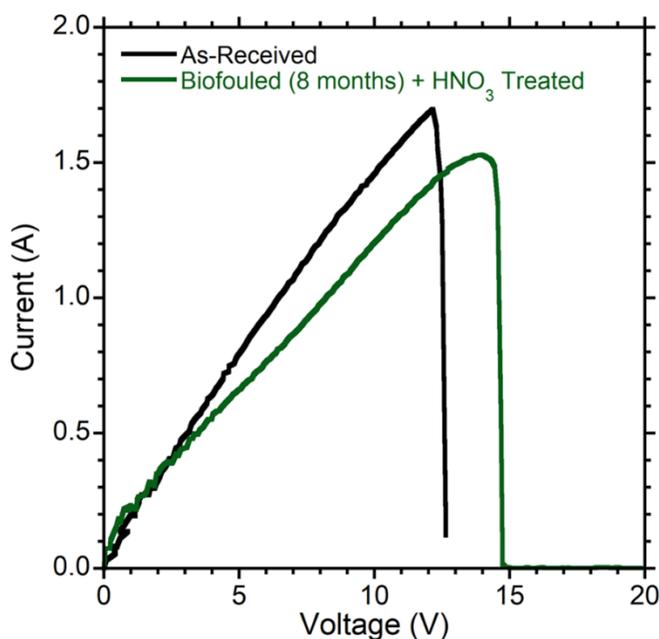


Figure S6. Current carrying capacity of an as-received CNT ribbon compared to an analogous sample after 8 months of ocean exposure and subsequent HNO₃ treatment.

After CCC testing, the CNT ribbon was analyzed by visual inspection and SEM. Figure S7 shows the as-received CNT ribbon after 8 months of ocean exposure, HNO₃ treatment, and CCC testing. The photograph demonstrates that unlike the as-received control (see Figure 6 in the main text), there is no necking or orange discoloration observed at the failure point. However, SEM analysis demonstrates that residual iron catalyst remains in the sample, and it is agglomerated at the failure point. These findings corroborate the earlier TGA results. Thus, while both the HNO₃ and HCl treatments are effective at removing the biogrowth that occurs on the CNT samples when deployed in the ocean, only the HCl treatment provides an added benefit of improving CNT purity as well.

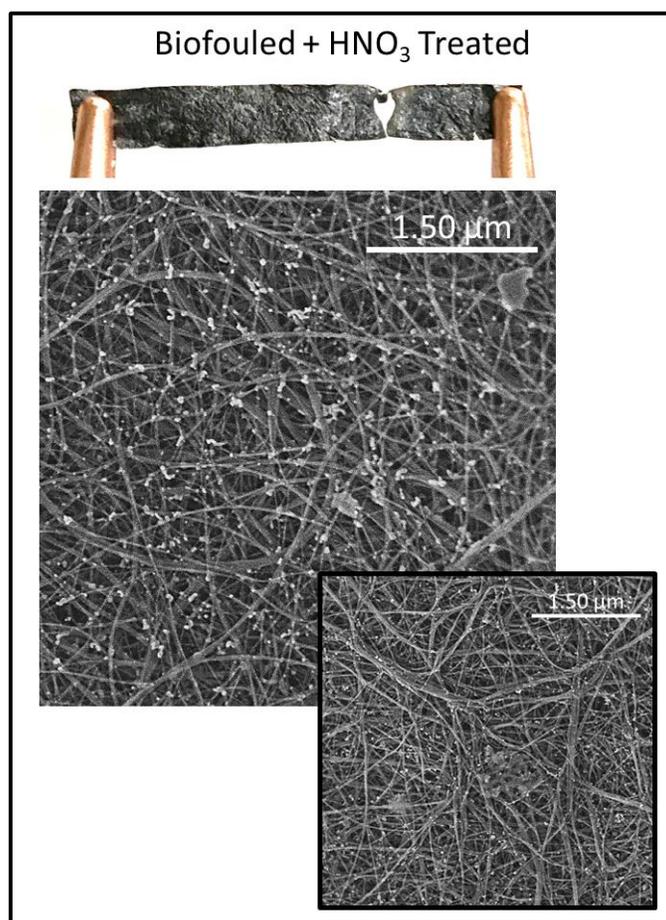


Figure S7. Photograph showing an as-received CNT sample after 8 months of ocean exposure and HNO₃ treatment after current carrying capacity testing. The corresponding SEM micrograph was obtained at the failure point, and the inset shows the CNT bulk away from the failure point.

References

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