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Functionalizing Carbon Nanotube Forests with 1,5-diaminoaphthalene

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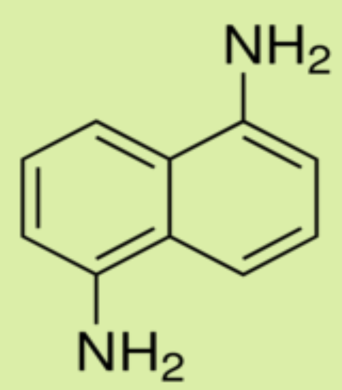
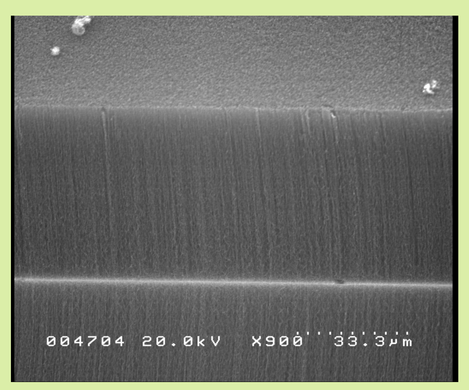
Motivation

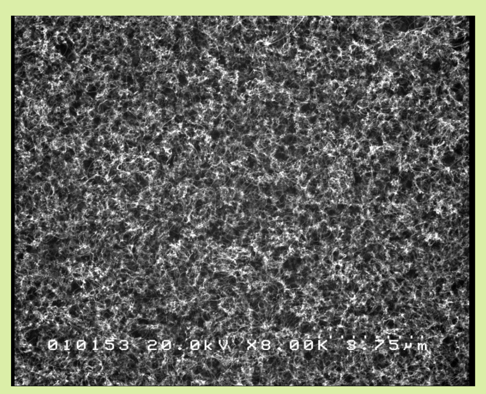


1,5 diaminonaphthalene (DAN)

- Extensive surface area of carbon nanotube (CNT) forest can provide more binding sites and enhance ELISA detection limit.
- A linker molecule is needed to bind to CNT non-covalently and bind to biomolecules covalently.
- Aromatic rings in 1,5-diaminonaphthalene (DAN) can form π-stacking bonds with CNT sidewall. [1,2]
- Need to characterize DAN concentration and optimize surface coverage on CNTs.

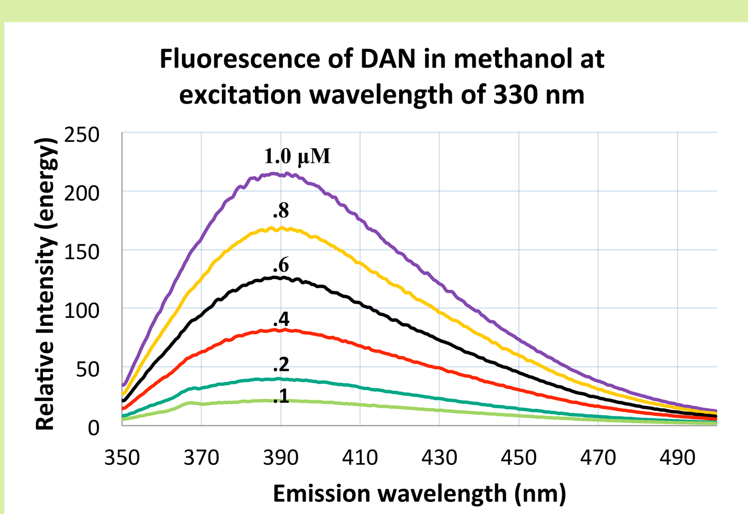


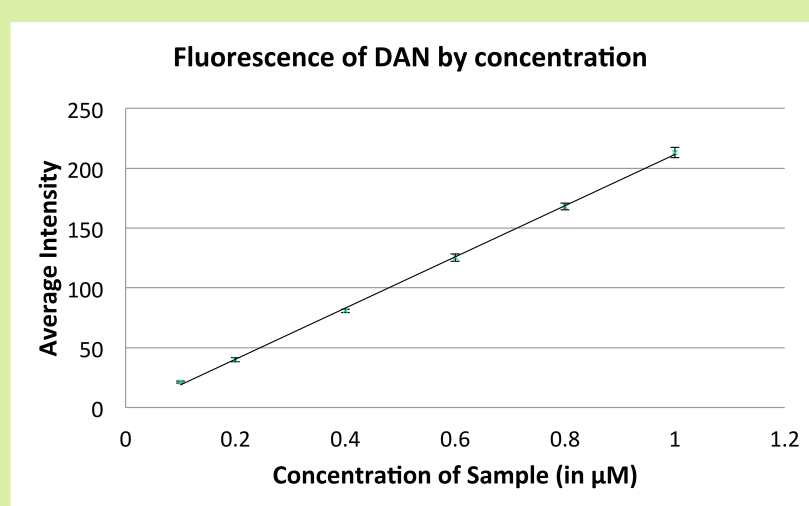
Carbon nanotube forest (side view)



(top view)

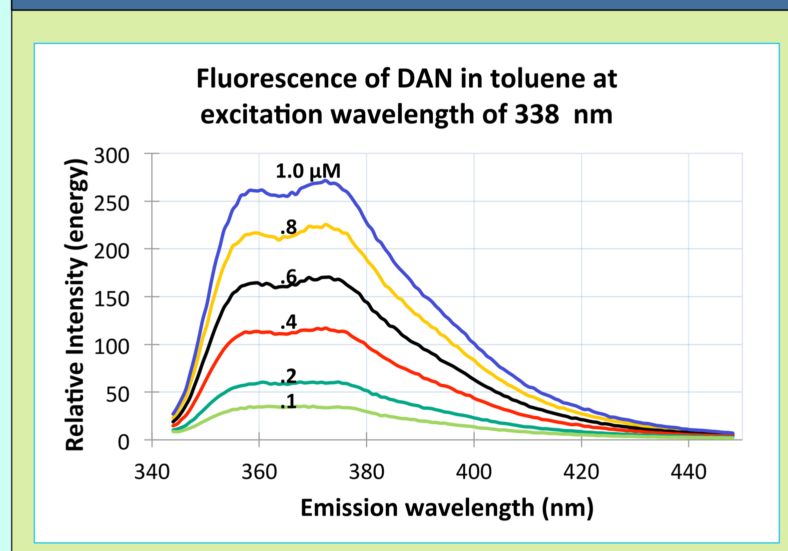
DAN in Methanol

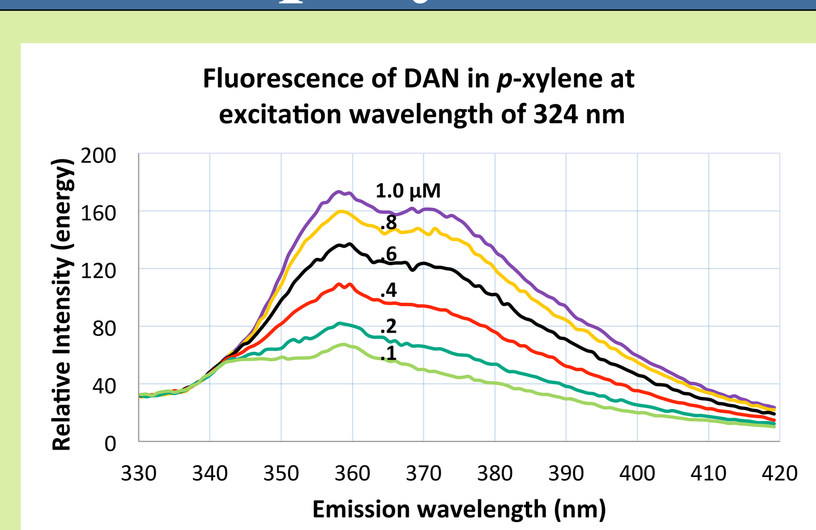




The fluorescence of DAN dissolved in methanol at various concentrations was obtained at an excitation wavelength of 330 nm. The peak emission wavelength for all concentrations is 390 nm. The peak intensity is linear with the concentration. The small peak seen at the emission wavelength of 360 nm at low concentrations is an artifact of the instrument.

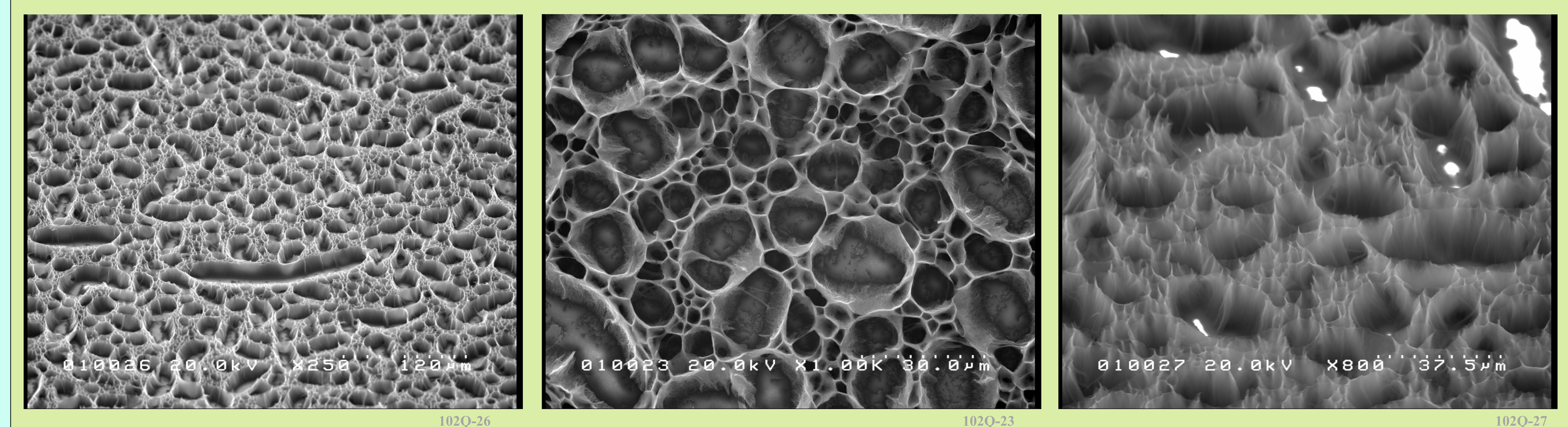
DAN in Toluene and *p*-xylene





To mimic the π- π interaction between DAN and CNT, we dissolved DAN in toluene and *p*-xylene. There is a significant amount of peak shift toward shorter wavelengths. For toluene, we observed a pronounced double peak in the emission spectrum at wavelengths of approximately 360 and 371 nm, at the best excitation wavelengths of 324 and 338 nm. For *p*-xylene at an excitation wavelength of 324 nm there are two prominent emission peaks of DAN at 360 nm and 370 nm, but only at high concentrations. At low concentrations, only the 360 nm emission peak remains.

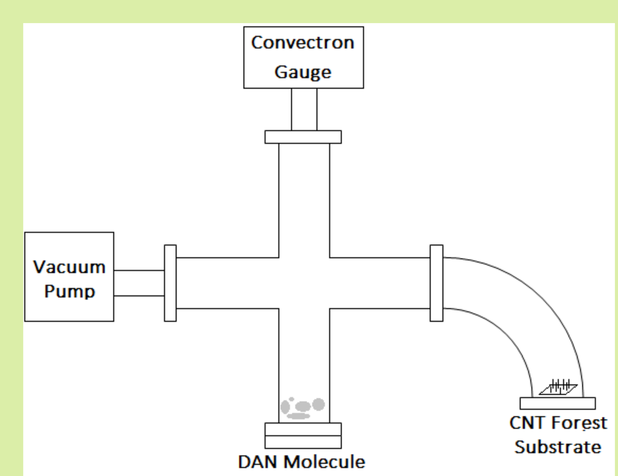
Liquid on CNT forests

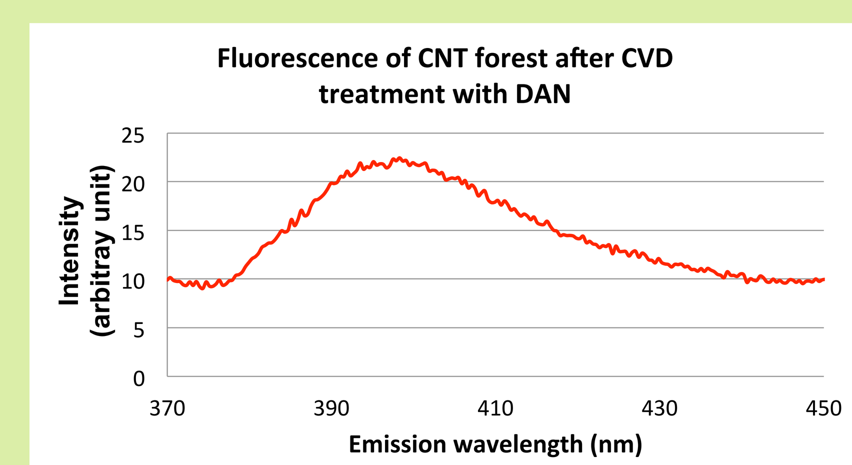


A CNT forest after soaking in DAN/methanol solution and air drying.

SEM images show that capillary force and evaporation of liquid can significantly alter the morphology of the CNT forest. The CNT forests will collapse by the capillary force and disappear after drying. Soaking CNT forests with liquid and drying in air has been reported first by Chakrapani *et al.* [3] and used recently to create ultra-dense CNT patterns. [4,5] Properly patterned CNT forest can maintain its shape after densification, where the outer layer can be functionalized by DAN and subsequently by proteins.

Chemical vapor deposition of DAN on CNT





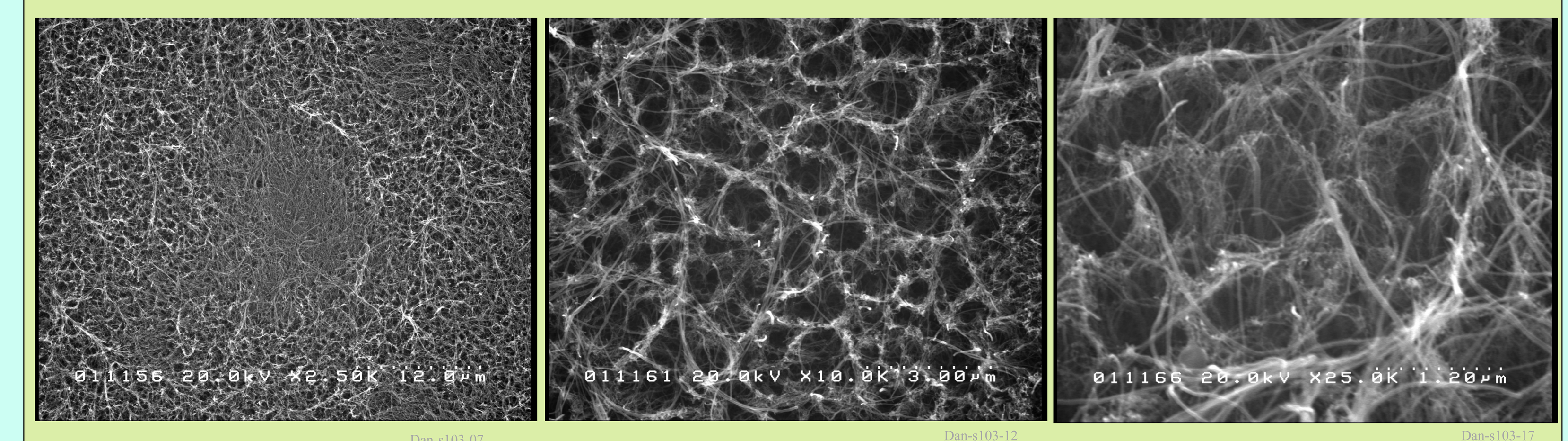
To eliminate solvent interaction with CNTs, we used a chemical vapor deposition (CVD) technique to deposit DAN directly on the CNT surface without the risk of solvent-induced capillary deformation. The chamber (shown above) was pumped down to 4.6×10^{-2} torr . The DAN was then heated to 250 ºC, and the CNTs were exposed to DAN vapor at 1.8 torr for 10 min. A fluorescence spectrum (shown above) was obtained using excitation wavelength of 326 nm, where a single emission peak centered at about 397 nm is observed.

Conclusions

- DAN can be detected by fluorescence in a variety of solvents. Its peak excitation occurs in the region of about 320-340 nm, and the emission wavelength can be measured by a single peak at 390 nm when dissolved in methanol and two peaks at 360 and 370 nm when dissolved in toluene and xylene .
- The relationship between fluorescent intensity and DAN concentration in solvents is linear in the small ranges that we tested.
- Crystals of DAN nucleate and grow on DAN and form 3-dimensional structures on top and within the CNT forest. We plan to investigate the crystal formation as a function of the CNT pillar spacing by photolithography.
- The capillary force can be used to make ultra-dense structures that are resistant to solvent effects. The final configuration of the structures is controlled by the CNT's initial configuration. These structures provide an ideal platform for DAN to bind to the CNTs, for eventual use in antigen detection.

DAN crystal interaction with CNTs

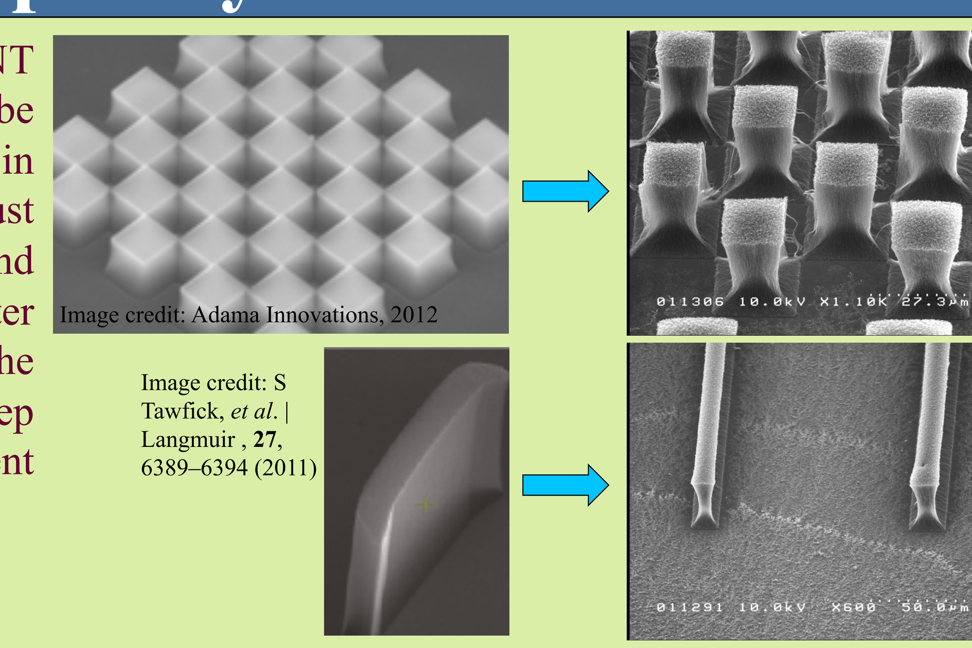
CNT bunching due to DAN crystal nucleation



DAN crystal formation on CNTs

Photolithography and the Capillary Force

By defining a pattern for CNT growth, the capillary force can be used to densify the CNT forest in predictable ways into very robust structures [6]. After patterning and growing the CNTs, we put 1 μL water on the sample and let it air dry. The CNT structures were found to keep their shape, even after subsequent cycles of wetting and air drying.



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Acknowledgements

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