# Fabrication and Chromatographic Separations on Binder-Free, Carbon Nanotube-Fabricated TLC Plates

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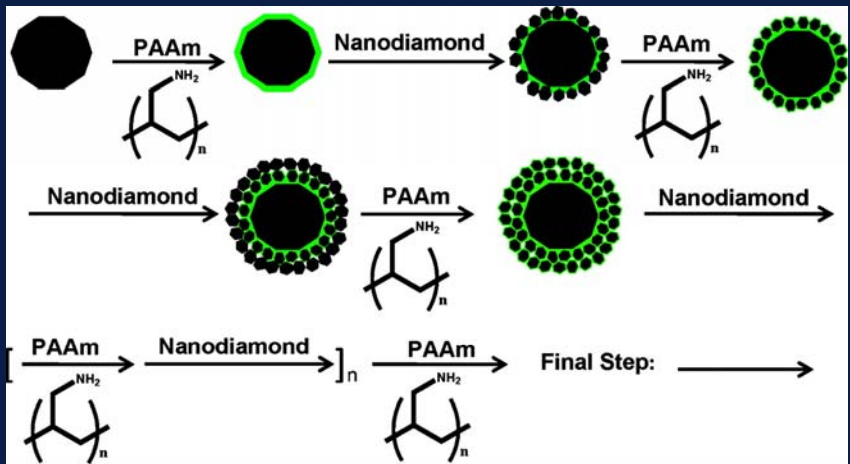
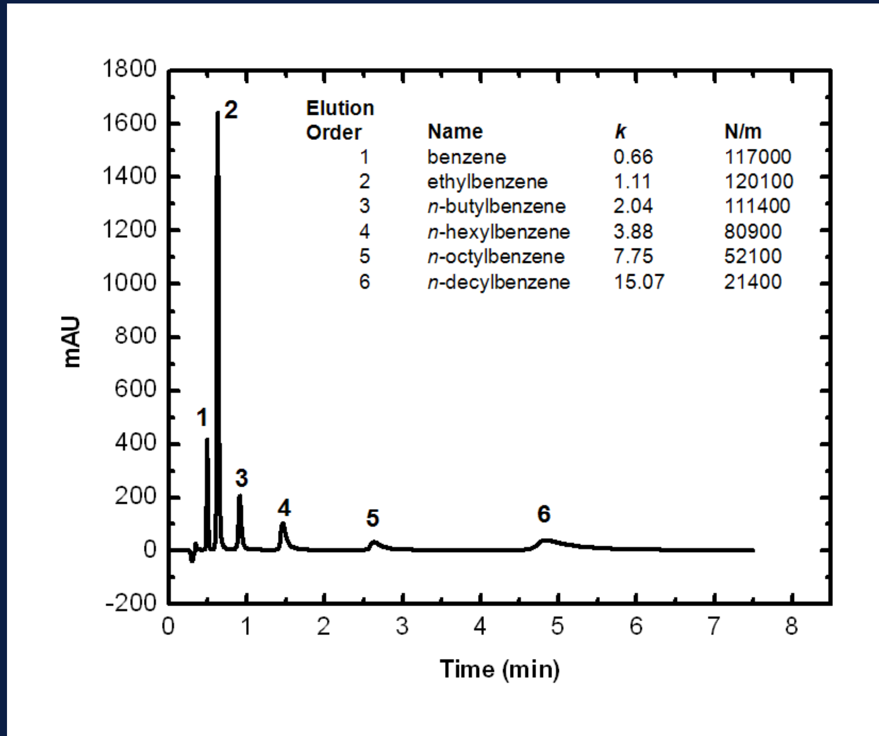
Preliminary work in this area published: Song, Jensen, Hutchison, Turner, Wood, Dadson, Vail, Linford, Vanfleet, Davis "Carbon Nanotube-Templated Microfabrication of Porous Silicon-Carbon Materials with Application to Chemical Separations"
*Advanced Functional Materials* **2011**; *21(6)*, 1132 – 1139

# Work in the Linford Group: New Materials for Liquid Chromatography: Layer-by-Layer (LbL) Formation of Core-Shell Particles with High Stability Materials



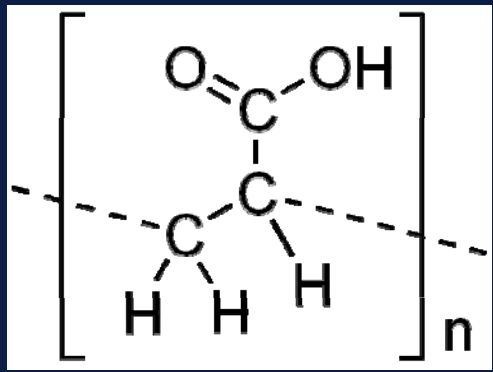




Saini, Jensen, Wiest, Vail, Dadson, Lee, Shutthanandan, Linford
*Anal. Chem.*, **2010**, *82* (11), pp 4448–4456: Diamond on diamond

Wiest, Jensen, Hung, Olsen, Davis, Vail, Dadson, Nesterenko, Linford
*Anal. Chem.*, **in press**: Diamond on spherical glassy carbon cores

# Why microfabricate a (binder-free) TLC plate

- TLC and HPTLC plates are produced by casting a slurry of particles
- TLC plates contain a binder
  - Low molecular weight polymer (PAA)
  - Calcium sulfate (gypsum)
- The binder can interact with analytes
- Poole has observed that while little study has been made of this issue in the literature, the binder may very well block the pores of the particles and contribute in a noticeable way to the *C*-term of the van Deemter equation for conventional TLC plates
  - This seems reasonable



# Why microfabricate a (binder-free) TLC plate?

- Microfabrication allows for precise placement of features
  - Creation of a homogenous chromatographic bed
  - Possible reduction in analysis time
  - Improvement of chromatographic characteristics
- Computer simulations have demonstrated greater efficiencies with a more homogeneous adsorbent bed[1,2]
  - This should come as no surprise
  - and should lead to improvements in the *A*-term (packing regularity) and probably the *B*-term (fewer channels/imperfections in the packing)
- So precise placement of chromatographic features for TLC without a binder could improve all three terms of the van Deemter equation

1. De Smet, J. et al. *Anal. Chem.* **2004**, *76*, 3716-3726
2. Billen, J. et al. *J. Chromatogr. A* **2007**, *1168*, 73-99

# CNT Growth

$$xC_2H_{4(g)} + yH_{2(g)} + zAr_{(g)} \xrightarrow{750°C} CNTs$$

Because of steric constraints, nanotubes grow ca. perpendicular to the surface

However, the nanotube array is flimsy and by itself would be a useless device!

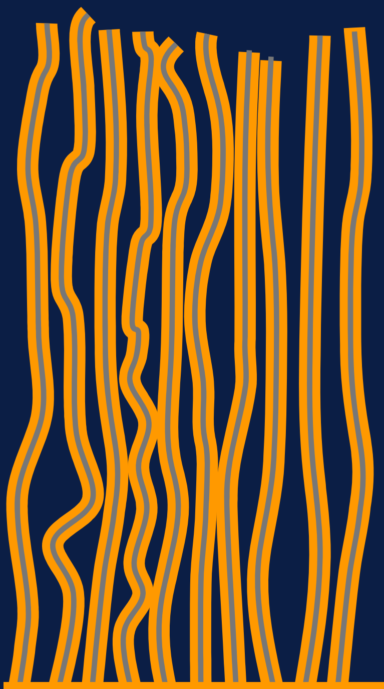
$$Fe \xrightarrow[H_2,\ Ar]{750^oC} Fe\ nanoparticles$$

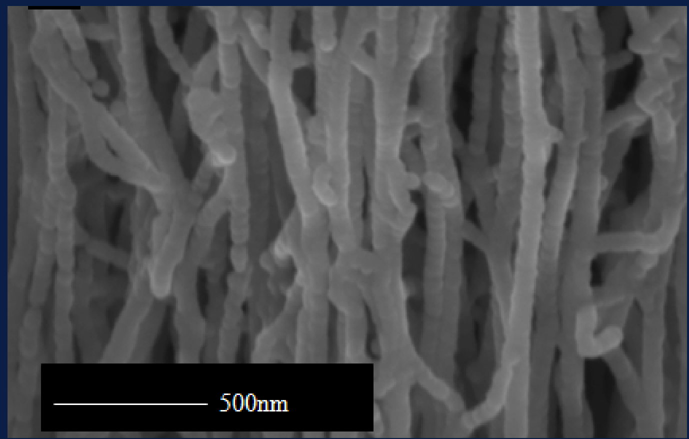

$Al_2O_3$ (Diffusion barrier, limits the formation of iron silicide)

Backing Material (Silicon wafer)

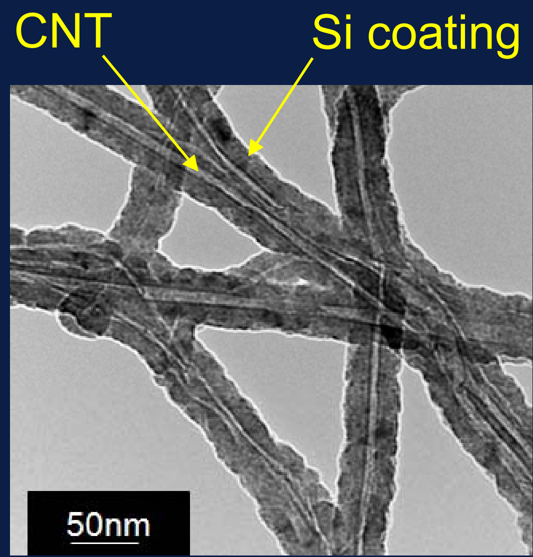
# Coating the CNTs with Silicon

$$SiH_{4(g)} \xrightarrow[10\ \text{mtorr}]{530°C} Si_{(s)} + 2H_{2(g)}$$

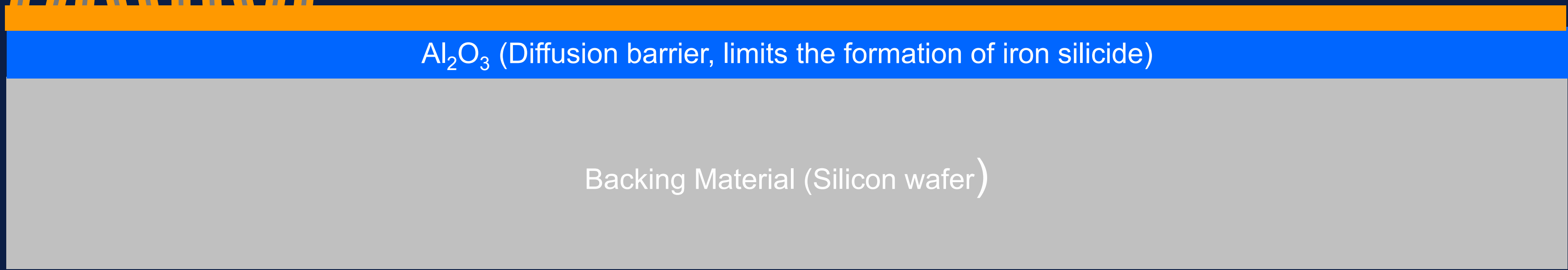





SE micrograph of silicon coated CNTs

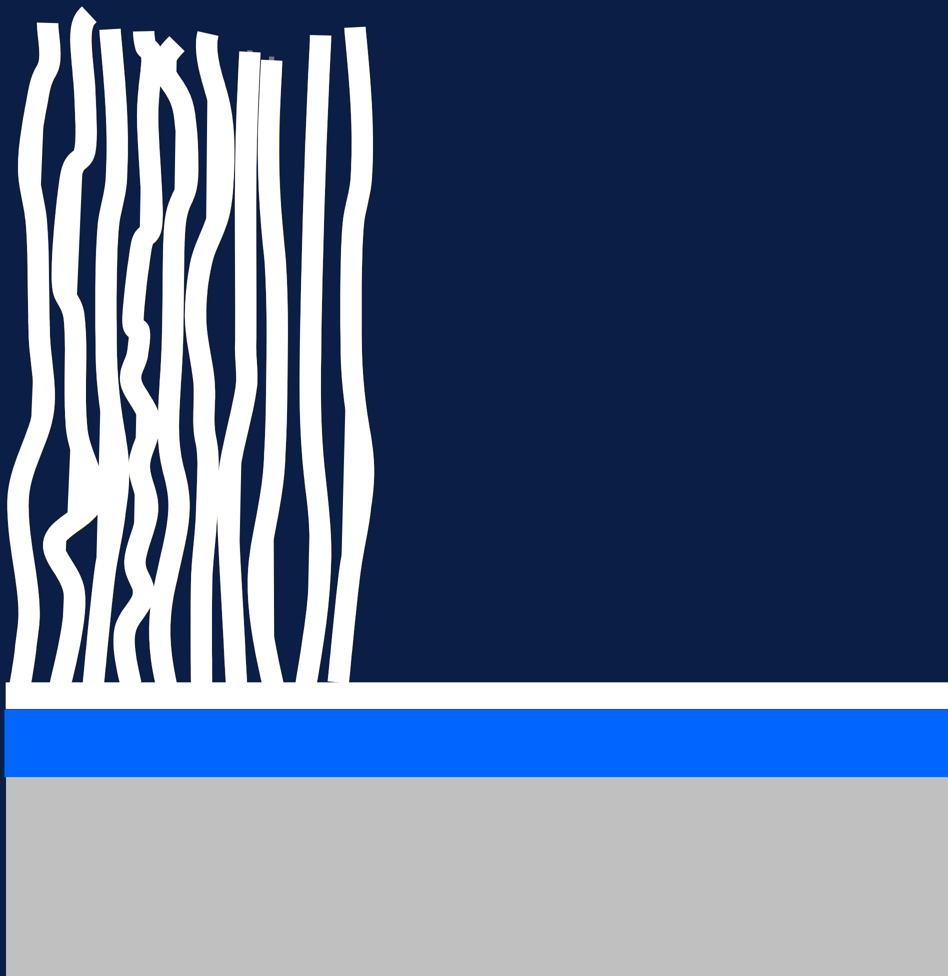


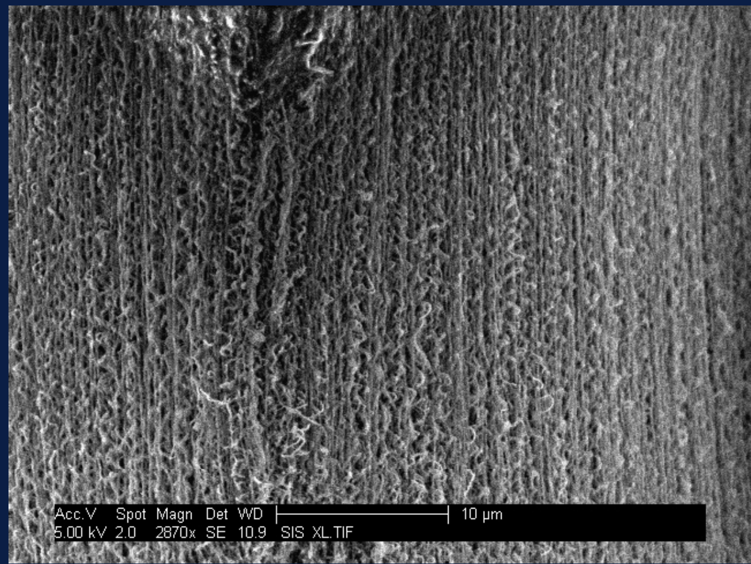

TEM image of silicon coated CNTS



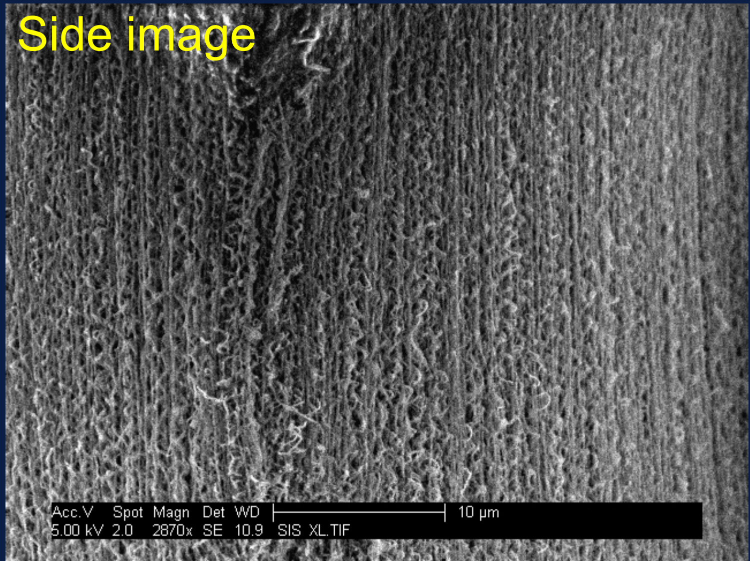
# Converting Silicon to Silica

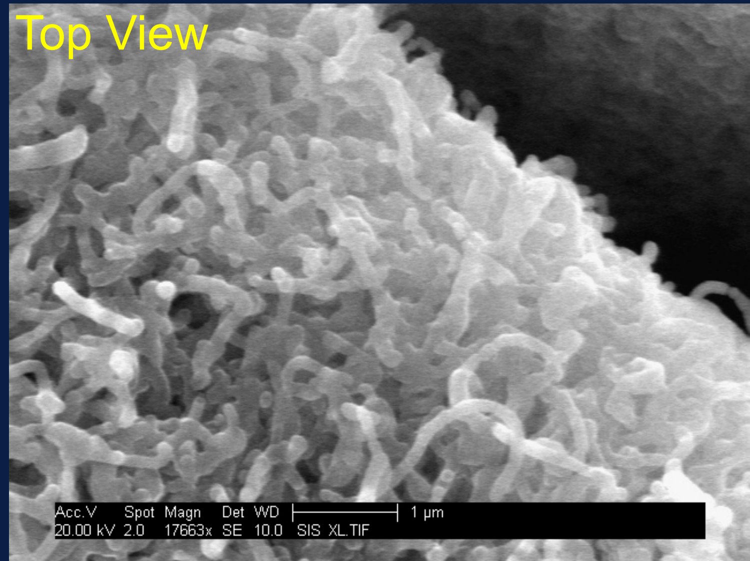
$$\text{Si - CNTs} \xrightarrow[\text{Air}]{1000^{o}\text{C}} \text{SiO}_2 + \text{CO}_{2(g)}$$

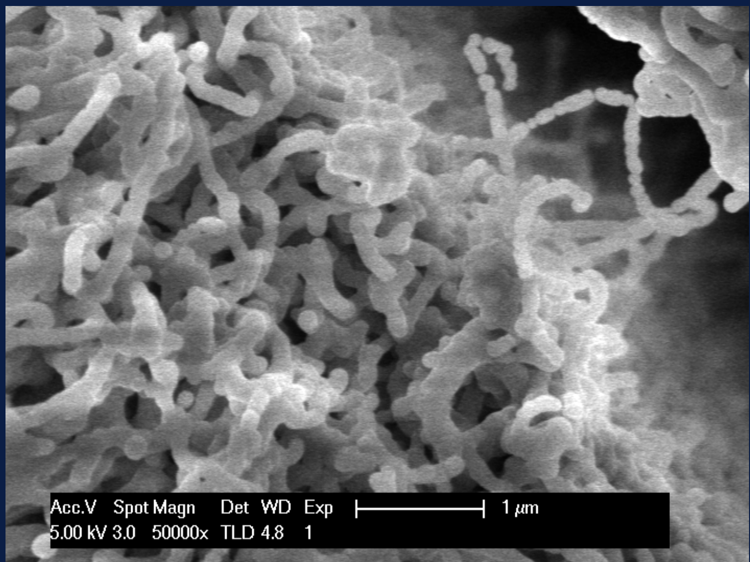


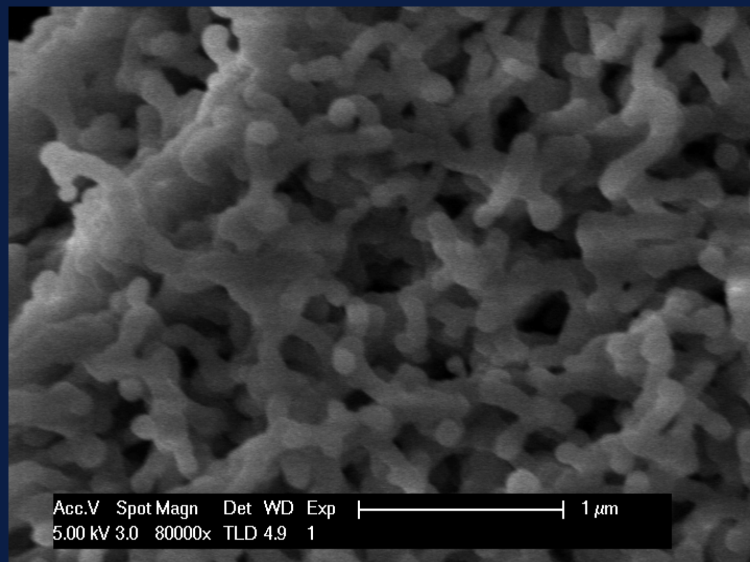


# SEM micrographs of the final product: High surface area silica materials

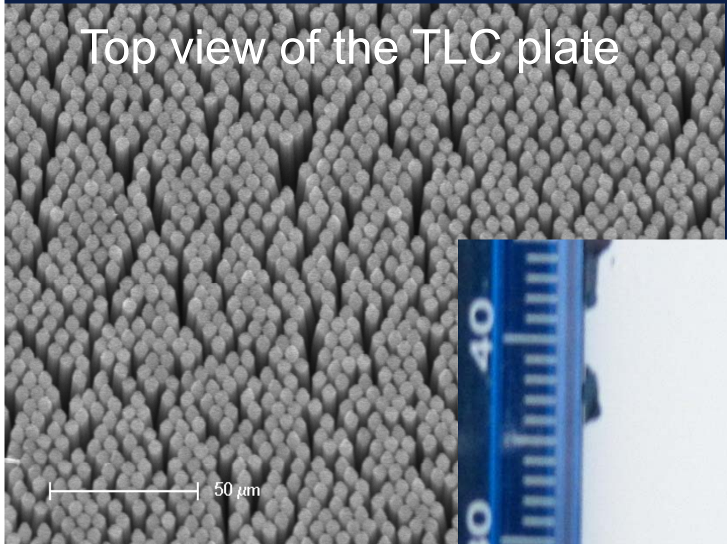


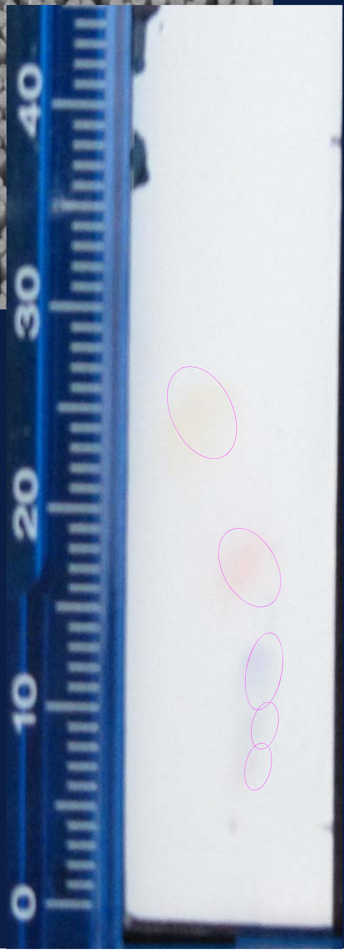



# Original Design: Pillar Array







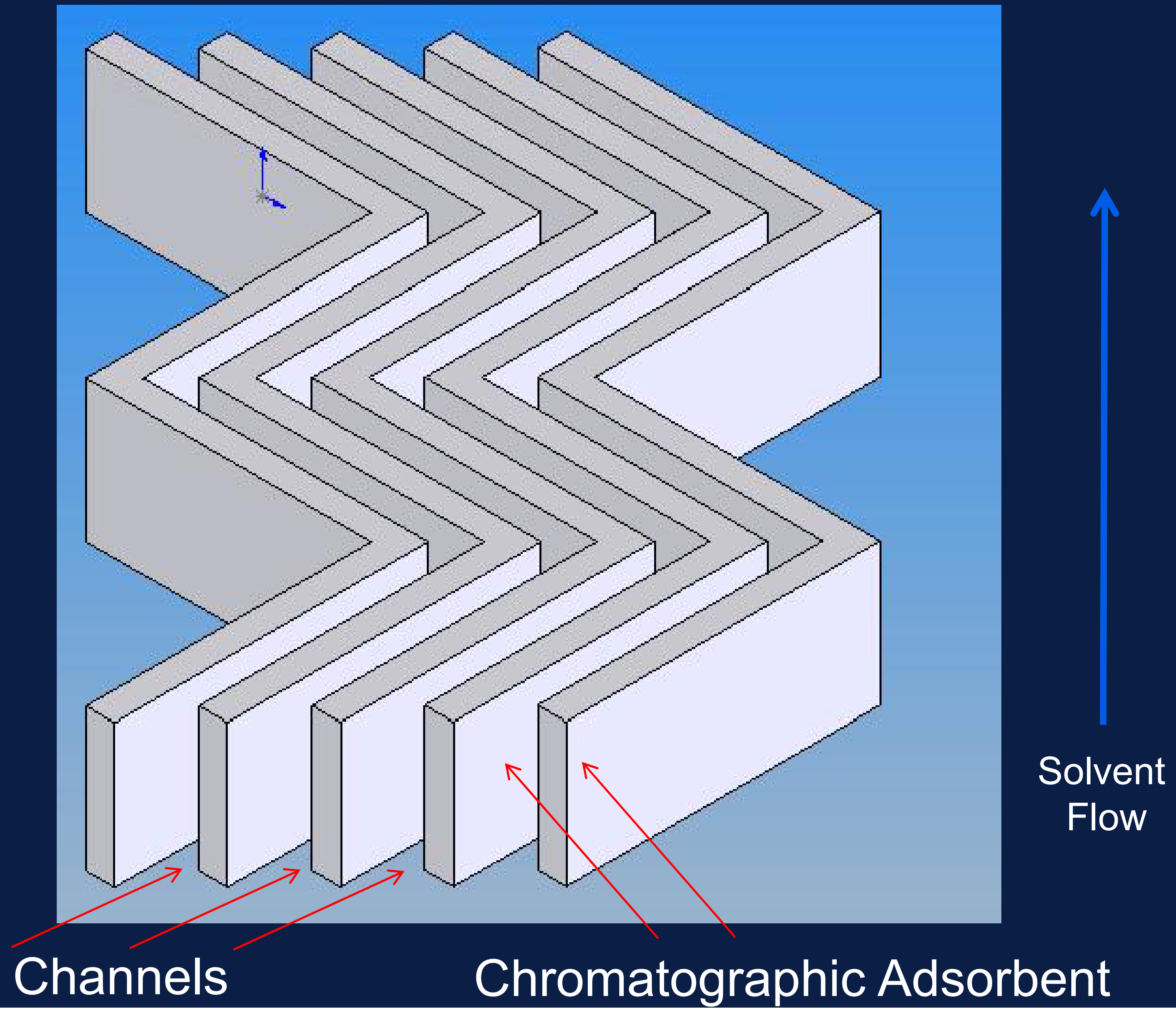

- Dimensions:
  10 x 5 µm pillars,
  100 µm tall
- This approximates work done by Regnier in 1998 on monolithic structures for microchip liquid chromatography
- CNT features lean when grown with large aspect ratios
- The plate did have some potential for chromatography
- But flow channels/irregularities in the beds
- In HPLC parlance: *A*-term problems – less than ideal separations

# What needs to be fixed?

- Silicon infiltration substantially increased the mechanical strength of the CNT framework
  - But the features lean
- Computational studies show that a parallel plate geometry gives the best theoretical plate height in chromatography[1,2]
- A zigzag pattern approximates a parallel plate geometry and prevents toppling

1. De Smet, J. et al. *Anal. Chem.* **2004**, *76*, 3716-3726
2. Billen, J. et al. *J. Chromatogr. A* **2007**, *1168*, 73-99

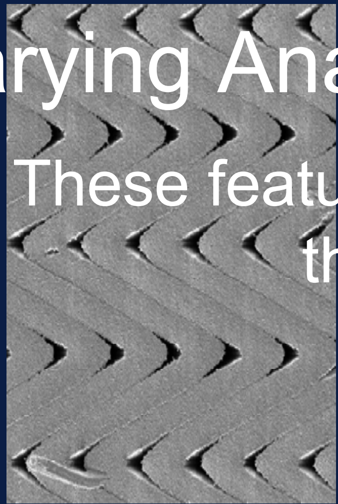
# Pattern Used



# Varying Analysis Time with Channel Width

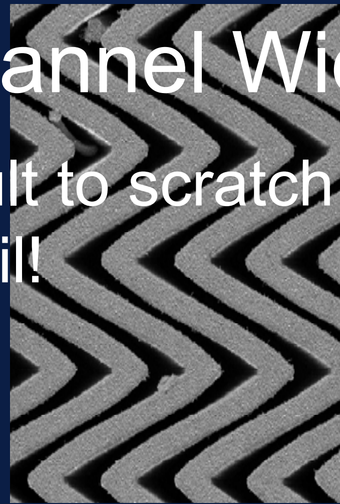
These features are robust! It is difficult to scratch them off with your fingernail!

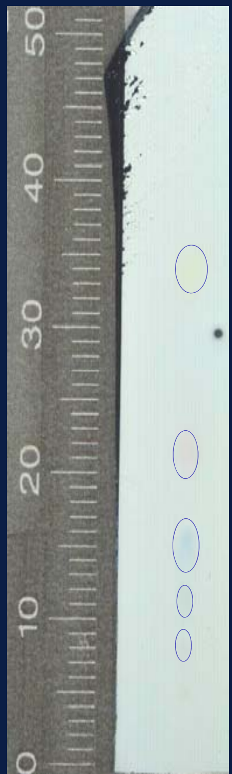
ca. 0 μm



2.5 μm

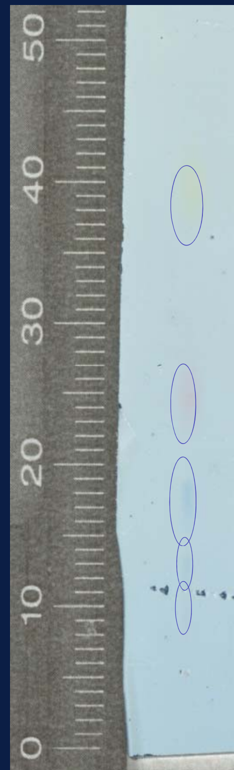
5 μm





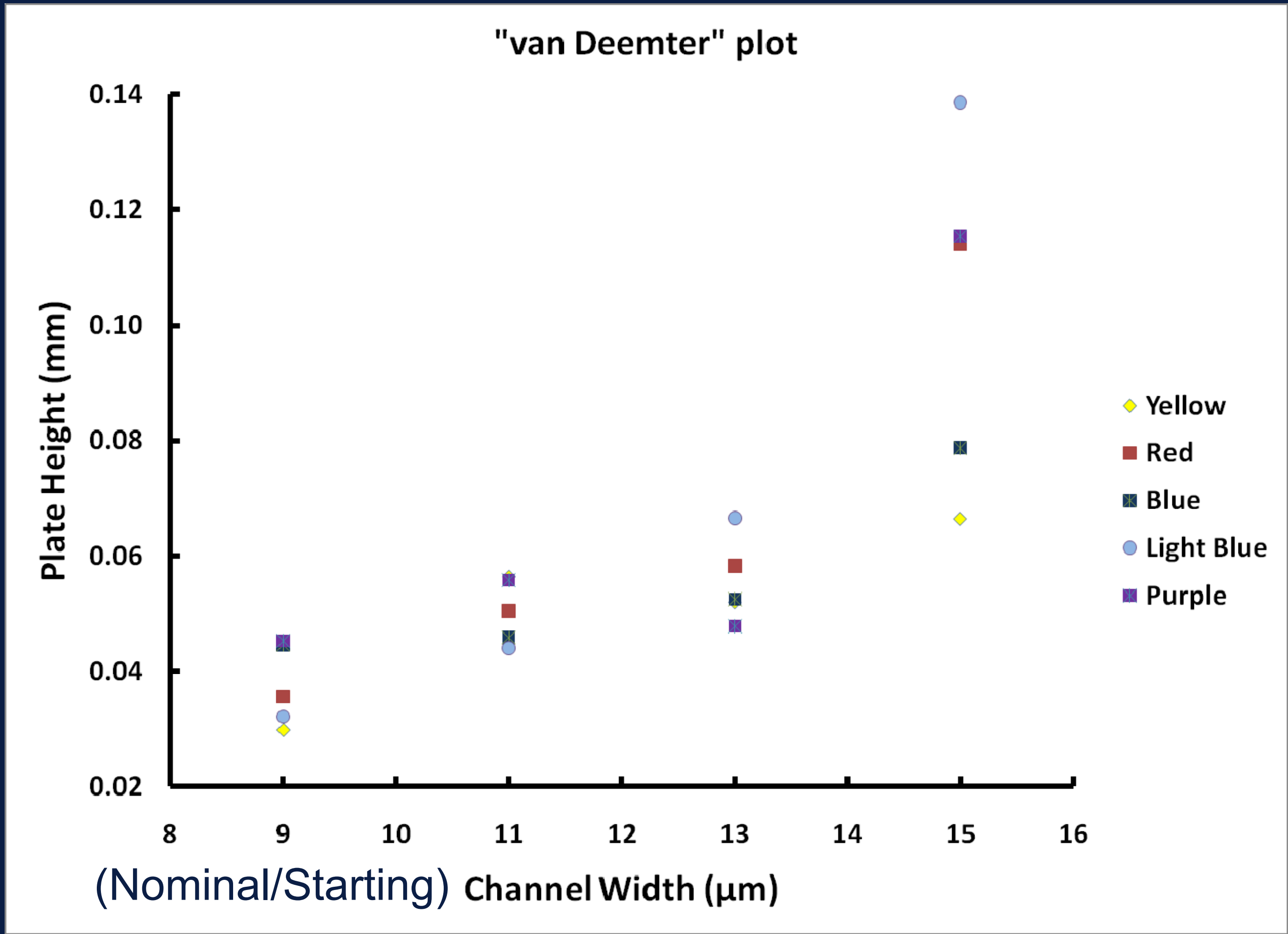

12 minutes


3 minutes




2.3 minutes

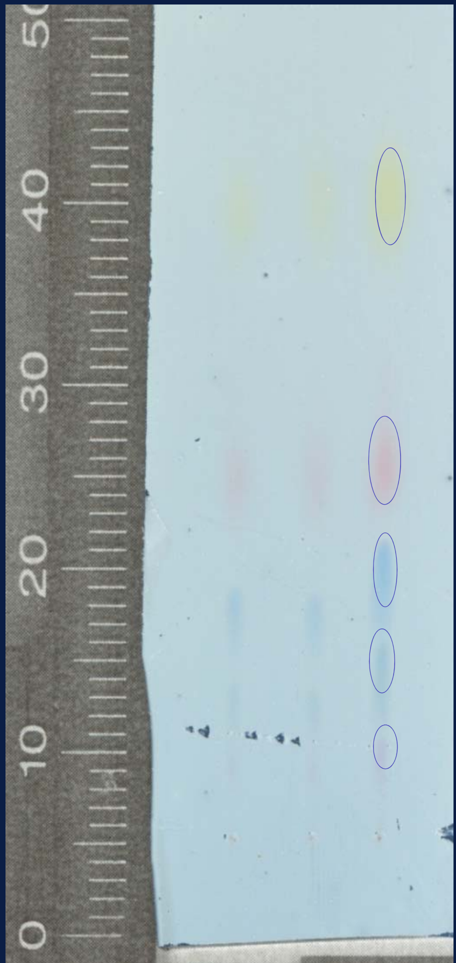
# Effect of Channel Width on Separation
## (increasing resistance to mass transfer)

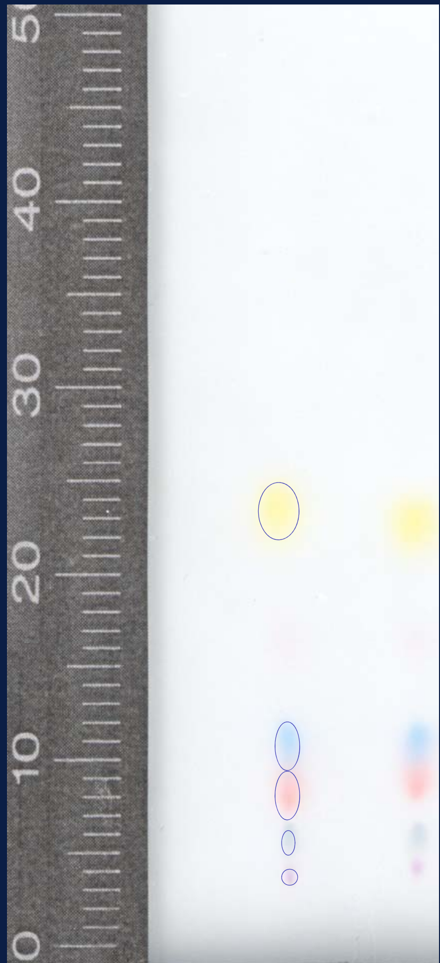


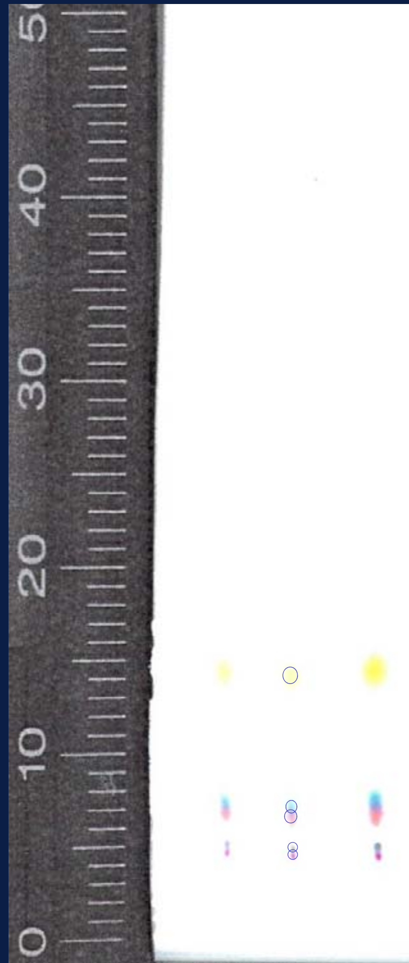
# Good Separations, Short Development Times

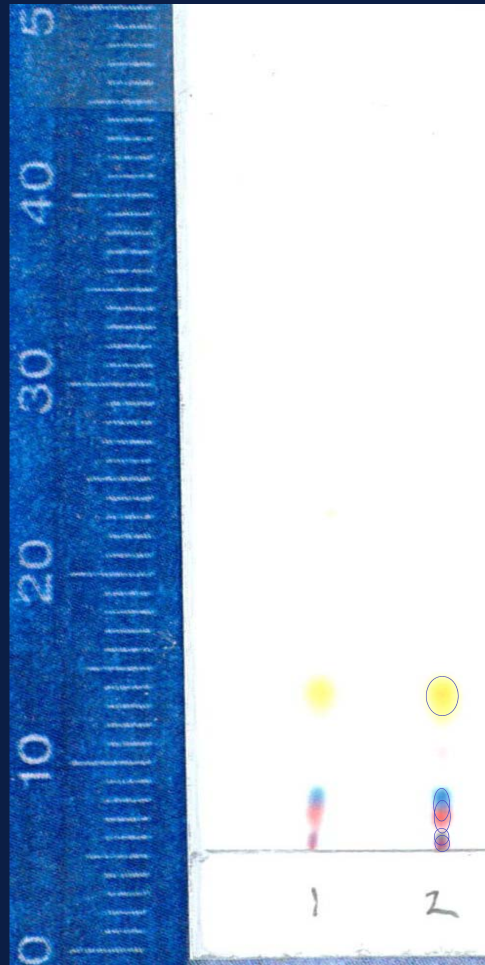
Run Times:

| 2 min 20 sec | 22 min 10 sec | 4 min 28 sec | 4 min 30 sec |
|---|---|---|---|





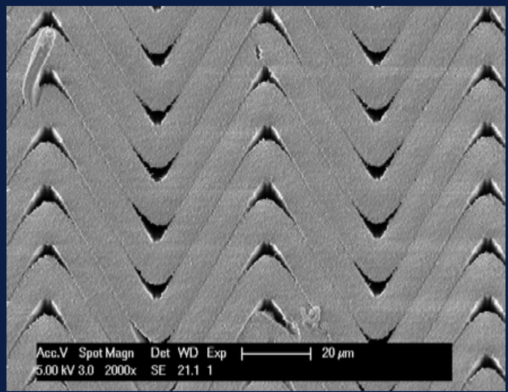


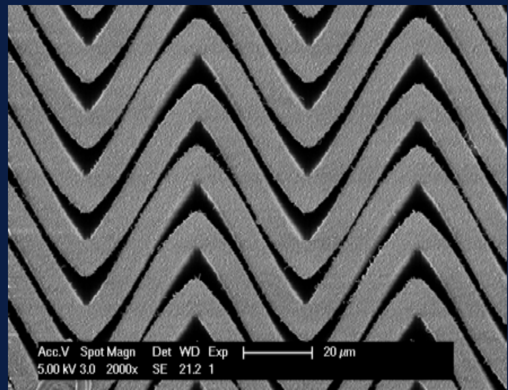


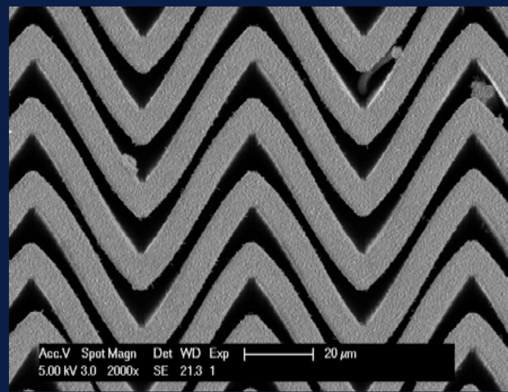
| Plate III CNT-M TLC (baseline separation) | Merck UTLC (baseline separation but long development time) | LiChrospher HPTLC (no baseline separation) | Merck TLC (no baseline separation) |
|---|---|---|---|

# Problem: Distortion of Features

- Feature distortion may lead to band broadening
  - Si to $SiO_2$ conversion causes distortion
    - "Swelling" of feature due to oxygen incorporation
    - Feature swelling hard to control



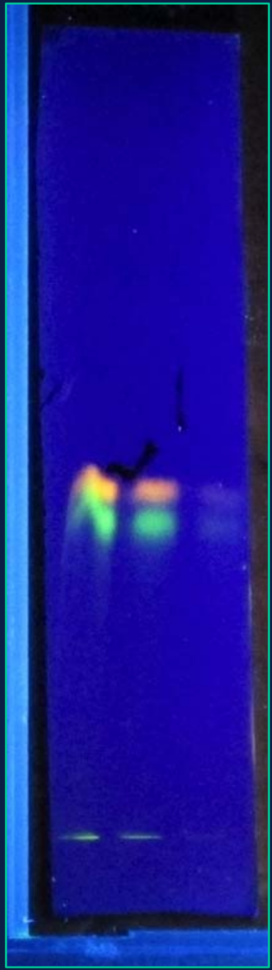

Features should look like this →

# Areas of Improvement

- Deal with distortion issue
- Increase in surface area for sample loadability
- Further optimization of channel width vs. adsorbent width
  - There are significant improvements that can still be made.
  - $H = A + B/u + Cu$
- Incorporation of fluorescent indicators
  - Detection at 254 nm and other wavelengths
- Surface silanization to produce different phases
  - $C_{18}$, $-C_8$, $-C_4$, $-NH_2$, -diol, -cyano, etc.

# Latest Results

- Amino Plate
  - Made with a process similar to the one described here
  - Green spot (Eosin Y) with 93,000 N/m and $R_f$ of 0.85
  - Orange spot (Sulforhodamine B) with 158,000 N/m and $R_f$ of 0.95
  - Run distance: 30 mm
  - Run time: 1 min. 10 s.



# Acknowledgements

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- US Synthetic Corporation (Orem, UT)
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