

INVESTIGATING THE EFFECT OF SUBSTRATE pH ON VERTICALLY ALIGNED CARBON NANOTUBE ARRAY (VANTA) GROWTH

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The role of water in super growth of vertically aligned carbon nanotube arrays (VANTAs) is not yet fully understood. Recent reports claim its role in retaining the active catalyst layer by slowing down particle coalescence and amorphous coke formation on the particle surface. A new study reports that water vapor changes the growth substrate acidity from lewis to bronsted, and discusses the promoting effect of a basic substrate in VANTA growth. Our research investigates the effect of altering pH of the growth substrate based on recent literature that uses the solid-state growth mechanism to explain its findings. The substrate is a silicon wafer with alumina deposited by atomic layer deposition (ALD) and sputter deposited Fe catalyst. Substrate pH will be altered over a range of 12 to 4 by dipping the wafers in various solutions of NH_4OH and HCl . VANTA growth is then carried out using C_2H_4 CVD at 750 °C and 1 atm pressure. Literature claims that basic supports catalyze and activate the growth of CNTs, especially compared to growth on acidic supports and we will use characterization techniques such as scanning electron microscopy and Raman spectroscopy to verify these claims.

Background

- To investigate the solid-state growth model of VANTA by chemical vapor deposition (CVD)
- Vapor-Liquid-Solid (VLS) Model**
- Carbon (C) and metal atoms condense from vapor to liquid
- Supersaturated C particles precipitate out of solution to form seeds for CNT nucleation

Vapor-Solid-Solid (VSS) Model

- Introduced to explain growth from metal catalysts that poorly dissolve carbon particles
- Proposes that C vapor condenses into solid (not liquid) fullerene-like carbon clusters that act as precursors for CNT growth
- Rao *et al.*¹ used nanodiamonds and fullerenes in ethanol (EtOH) to demonstrate SWNT growth by VSS
- Takagi *et al.*² also used nanodiamonds in EtOH
- Yu *et al.*³ used a C₆₀ derivative called fullerenedione in toluene

CVD Reactor

Growth conditions

- Temperature/time: 750°C, 10 min
- Gas flow rates:
 - Ar: 500 sccm
 - C₂H₄: 50 sccm
 - H₂: 100 sccm
 - Ar/H₂O: 10 sccm

Samples

- ~1 cm² chip of Si/SiO₂, 500 nm/Al₂O₃ (10 nm, ALD)/Fe (0.5 nm, sputter coat)
- Sample 1: Control
- Sample 2: A drop of CHCl₃ drop dried
- Sample 3: A drop of 0.25 g/mL C₆₀/CHCl₃ drop dried

Scanning Electron Microscopy (SEM)

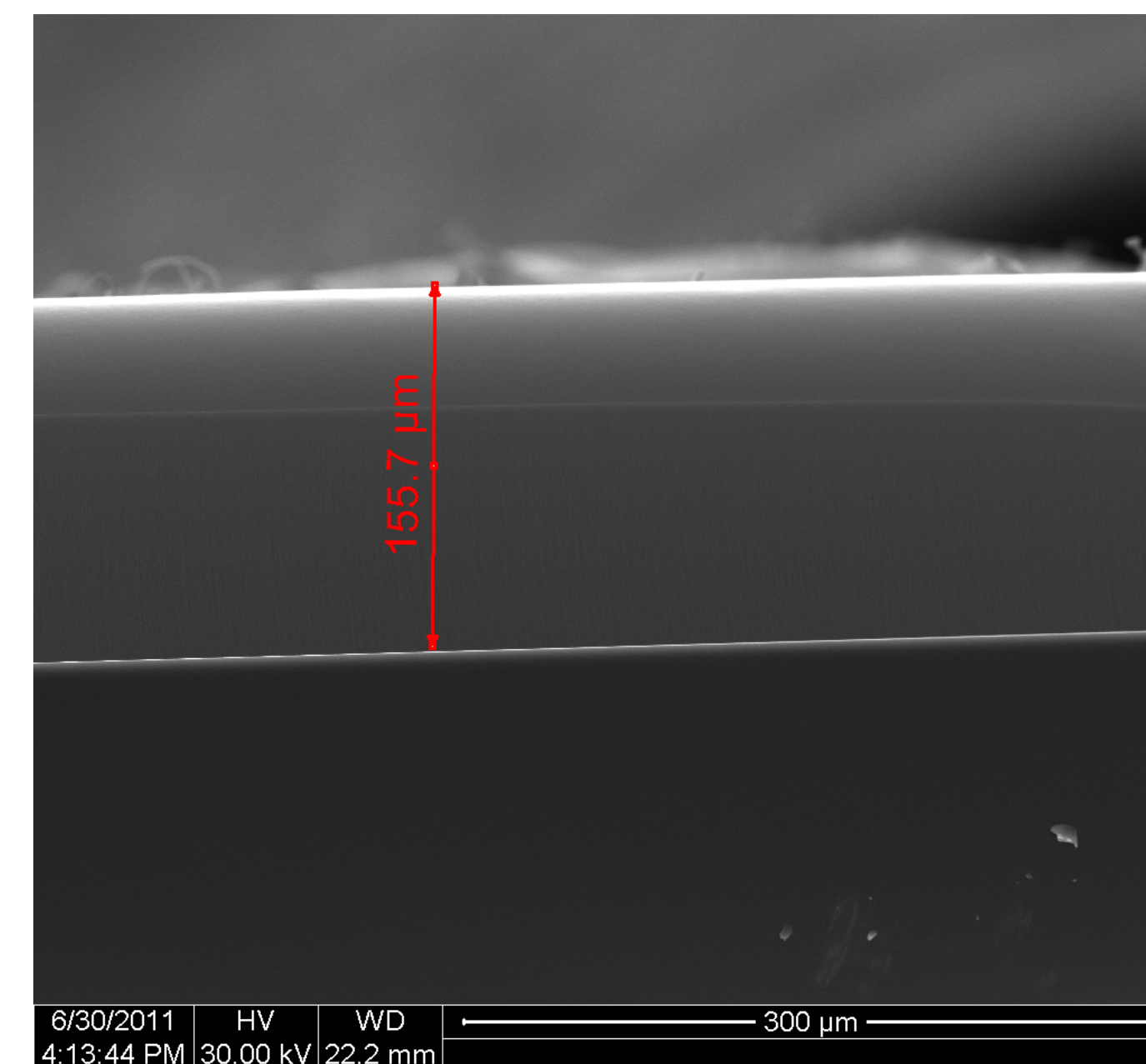


Figure 1

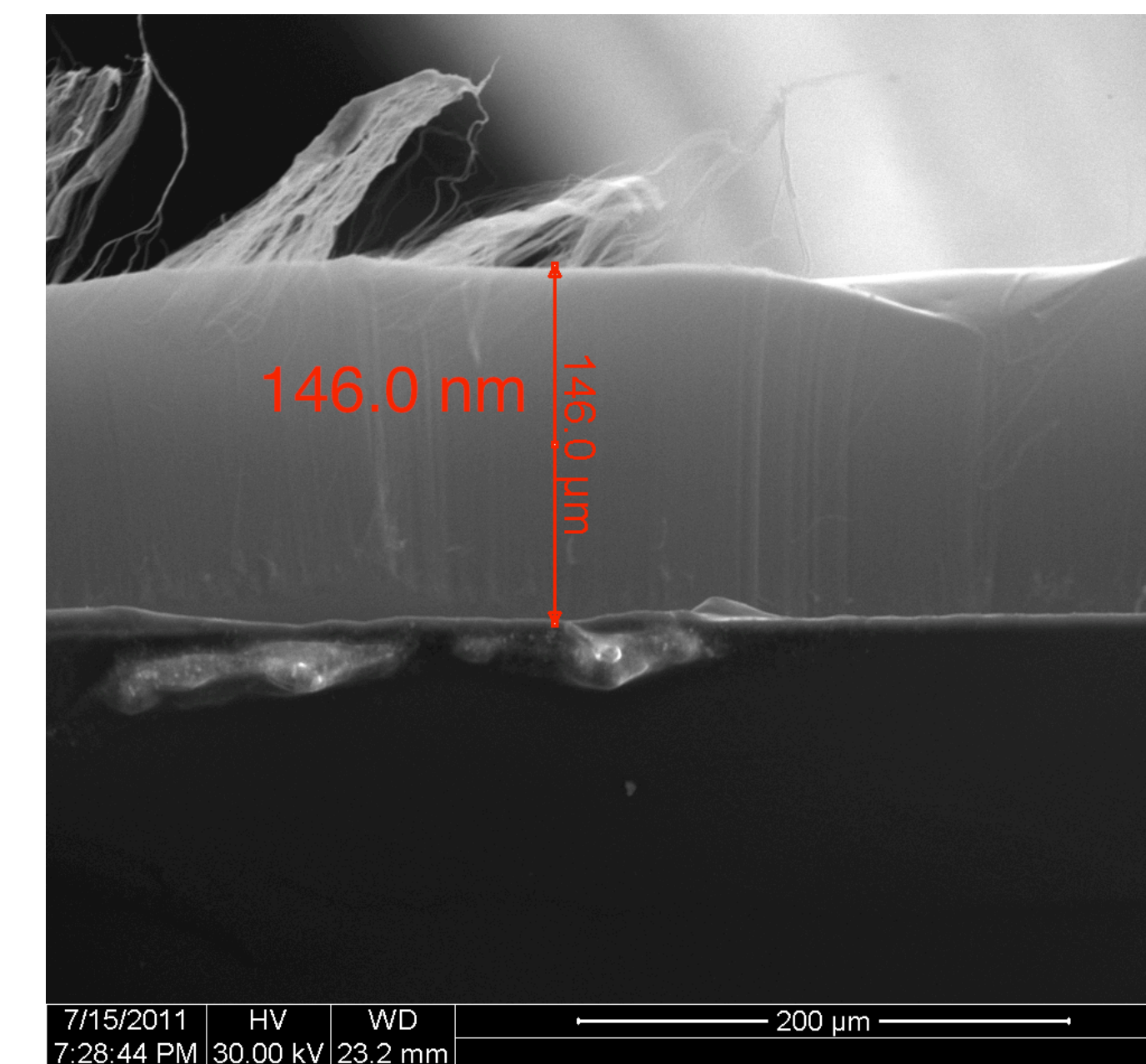


Figure 2

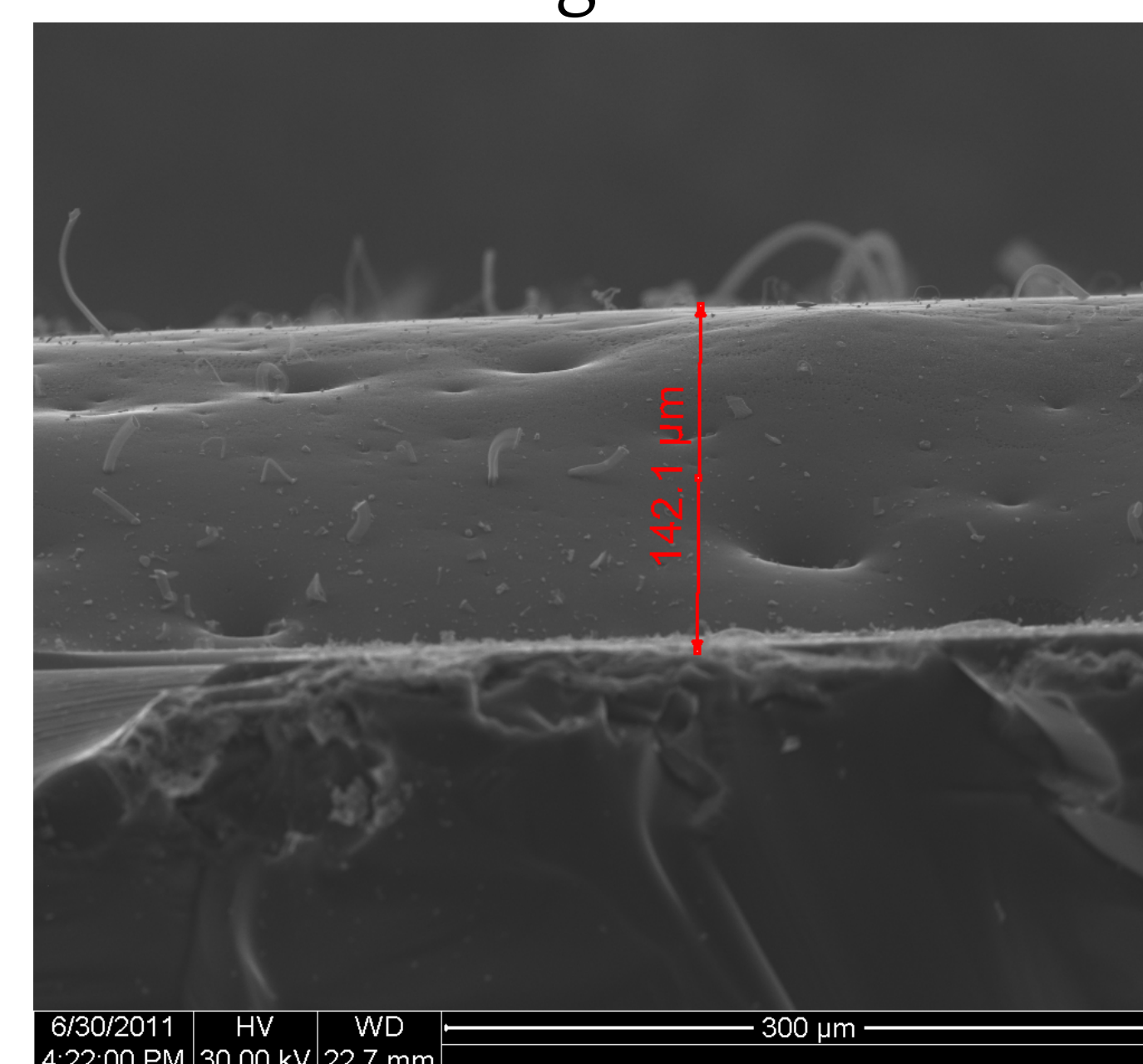


Figure 3

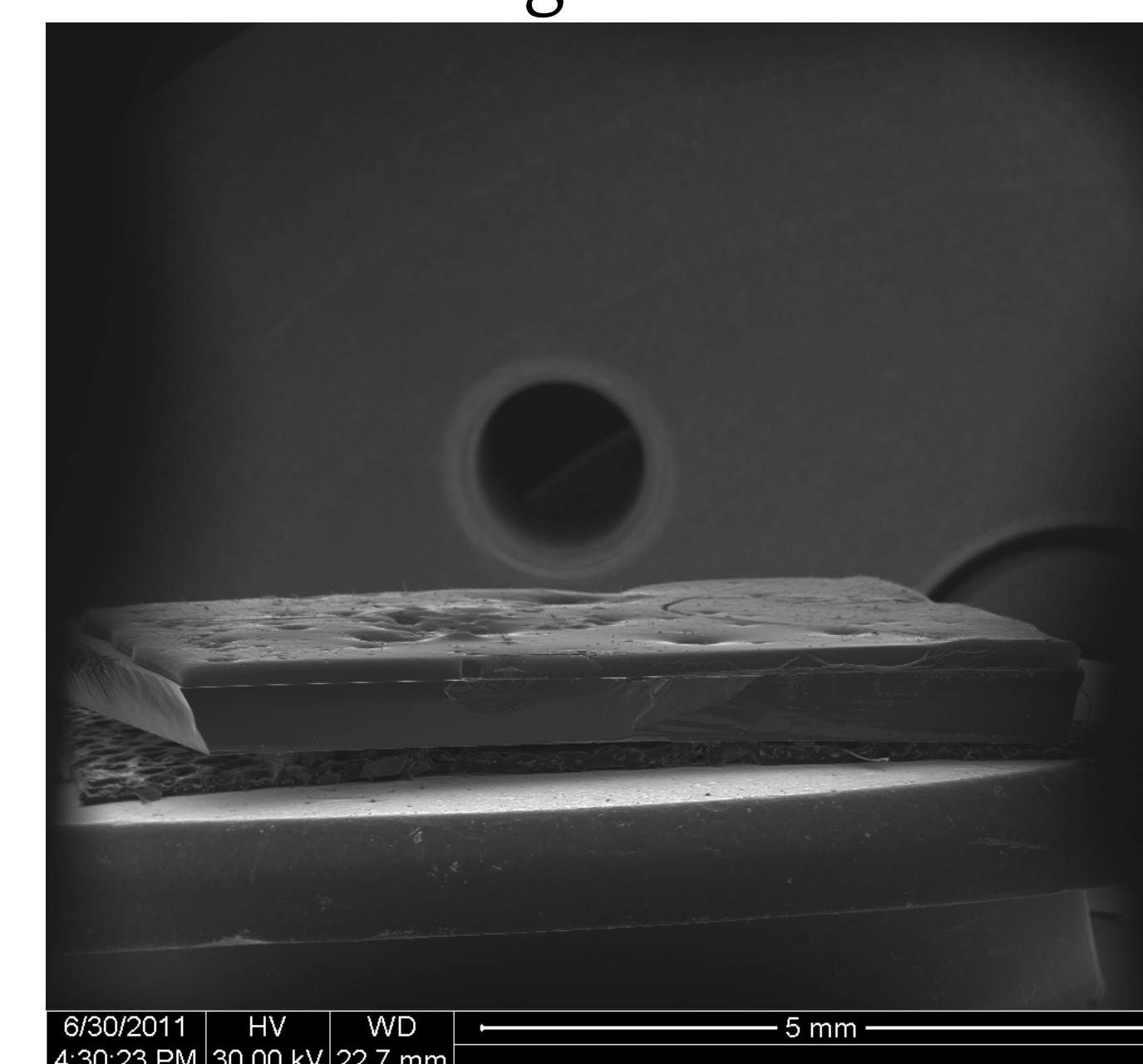


Figure 4

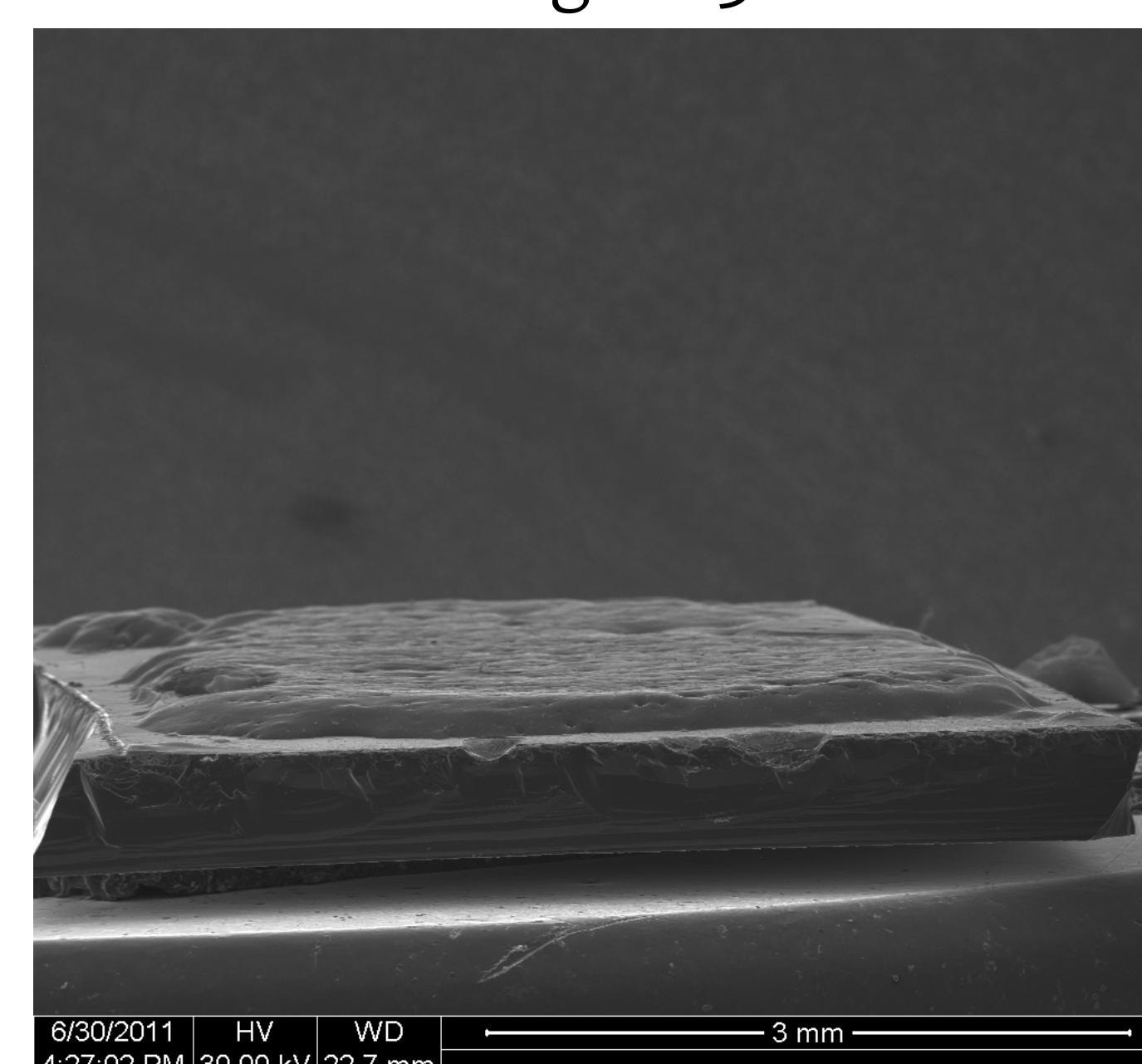


Figure 5

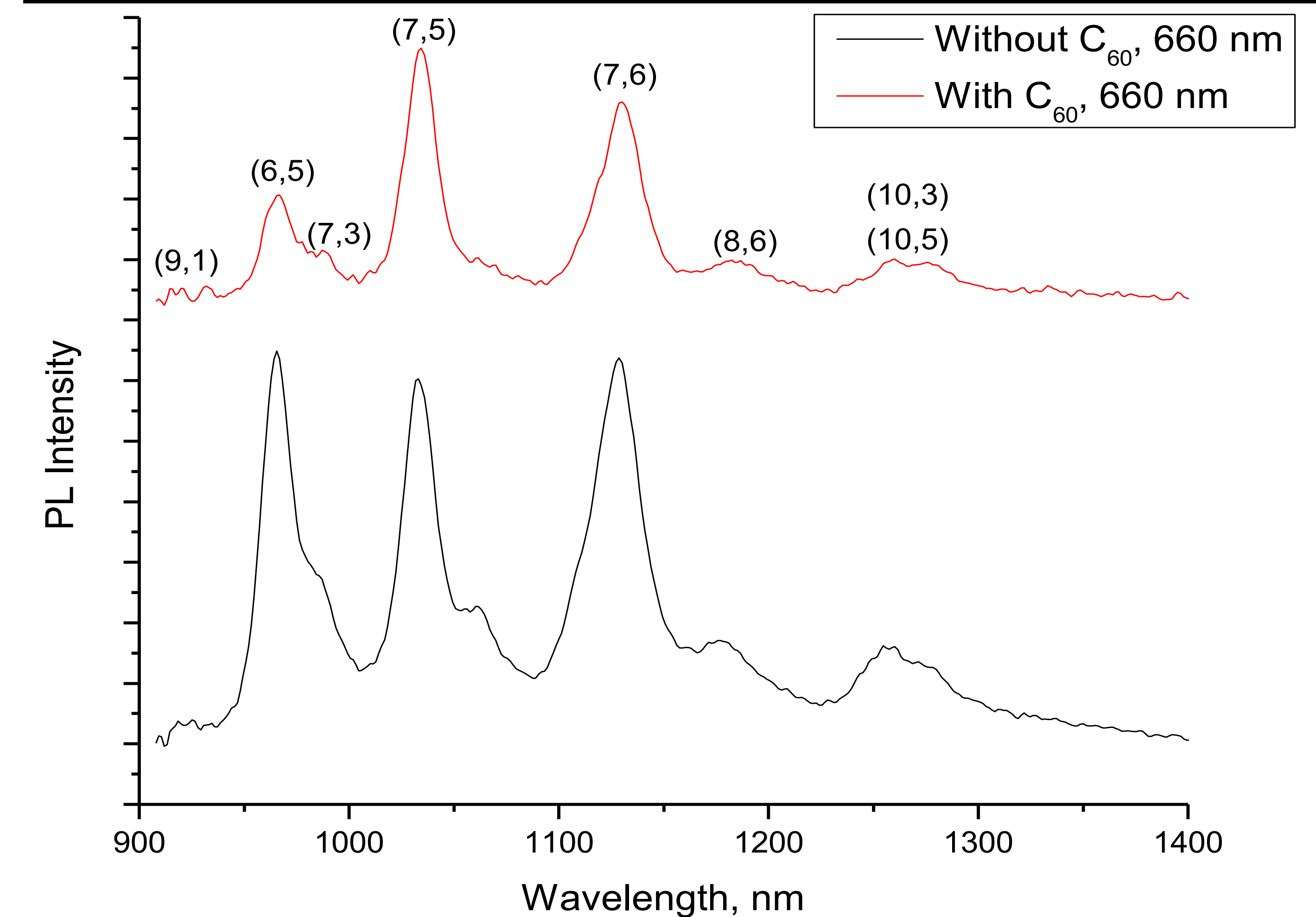
Figures 1-3 show average VANTA height: a) sample 1, 155.7 nm; b) sample 2, 146.0 nm; c) sample 3, 106.3 nm

Figures 4 and 5 show entire view of samples 1 and 3, respectively.

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Photoluminescence Spectroscopy



PL graph at 660 nm showing contrast between control solution (VANTA grown without C₆₀) and sample solution (VANTA grown with C₆₀) in 1 wt. % DOC.

Discussion

- PL shows significant change in SWNT chiral distribution
 - C₆₀ sample: spike in (7,5) peak compared to (7,6) and (6,5) peaks
 - Control: relatively even distribution of (6,5), (7,5), and (7,6) peaks
- Average length and height of SWNTs as obtained by atomic force microscopy (AFM) using SIMAGIS™
 - 780 ± 100 nm and 1.3 ± 0.4 nm, respectively
- Adding C₆₀/CHCl₃: does not appreciably change average VANTA height
- VANTA growth by CVD with added C₆₀ supports VSS growth

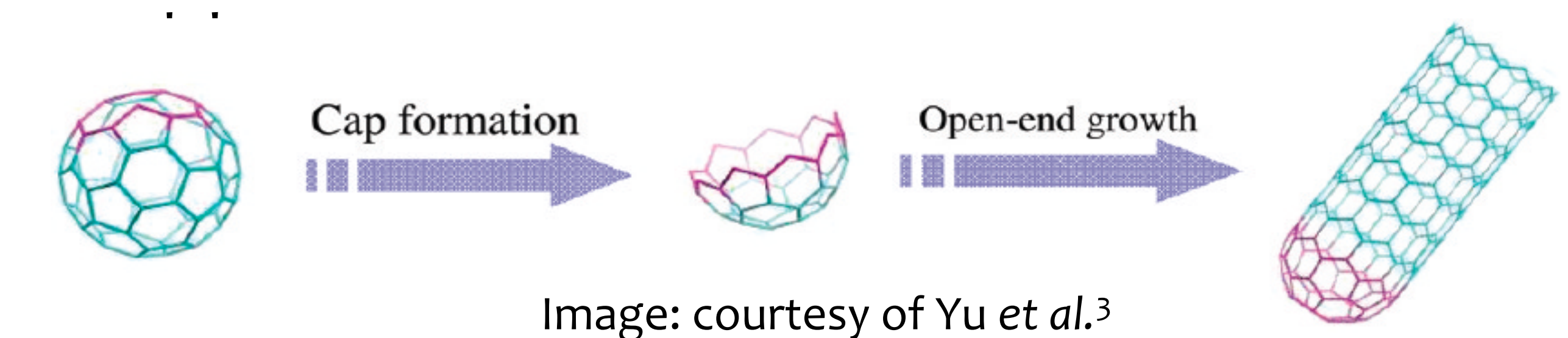


Image: courtesy of Yu *et al.*³

References

- F. Rao, *et al.*, *Carbon*, **47**, 3574 (2009).
- D. Takagi, *et al.*, **131**, 6923 (2009).
- X. Yu, *et al.*, *Nano Lett.* **10**, 3343 (2010).