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The growth mechanism of carbon nanotubes within the "cluster volume to surface area" model

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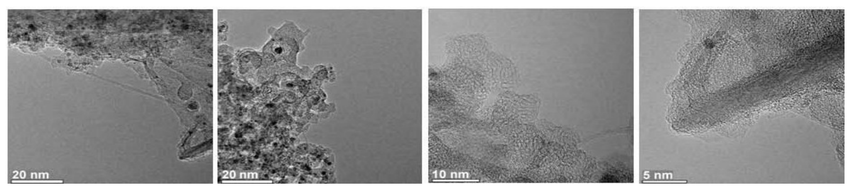
complex nano materials

Abstract

The influence of mixed catalysts for the high yield production of carbon nanotubes (CNTs) has been studied systematically. Based on extensive experimental data a “Catalyst Volume to Surface Area” (CVSA) model was developed to understand the influence of the process parameters on the yield and CNT diameter distribution [1,2]. In our study, we present a refined version of the CVSA model developed by combining experiments and simulations.

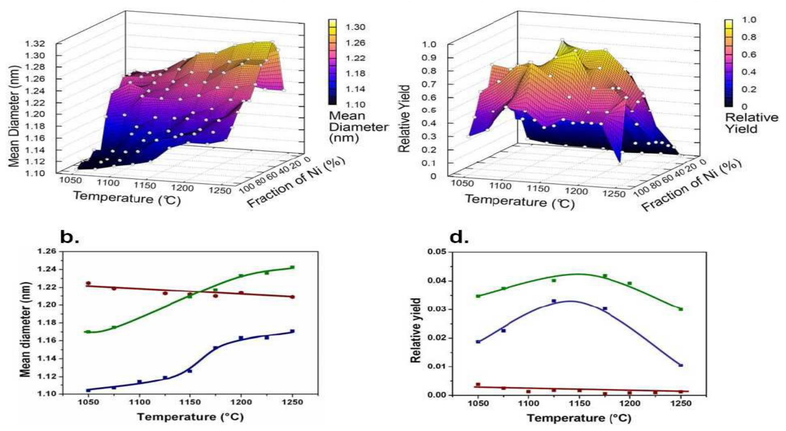
Experiments

- synthesis of carbon nanotubes (CNTs) by laser ablation with mixed catalysts



TEM images

- characterization of CNTs by optical absorption spectroscopy (OAS) [1]



CNT mean diameter relative yield

Motivation

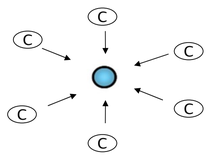
Want to understand the growth mechanism.

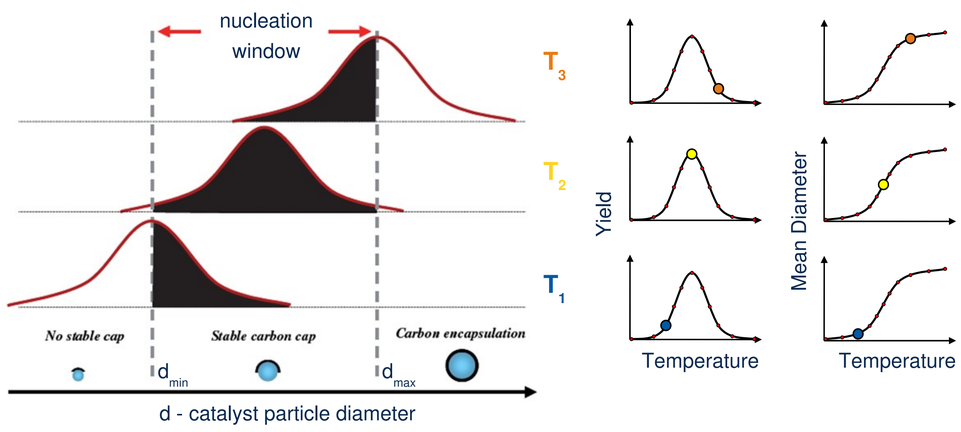
Strategy

- use “**cluster volume to surface area” (CVSA) growth model** [1,2]
- formulate the model mathematically
- fit measured data to the model and determine the model parameters
- interprete the model parameters in terms of microscopic quantities

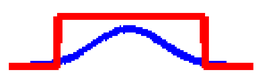
Growth Mechanism of Carbon Nanotubes (CVSA)

- after laser evaporation carbon dissolves into the catalyst particle and a liquid metal-carbide is formed
- the bigger the particles the more carbon is inside
- during the condensation carbon precipitates via the surface
- for CNT nucleation, formation of hemispherical cap is necessary
- the catalyst particle size increases with furnace temperature. Why?
  - during cooling the catalyst particles condensate
  - the higher the temperature the longer is the cooling time





Results: Mathematical Formulation of the CVSA model



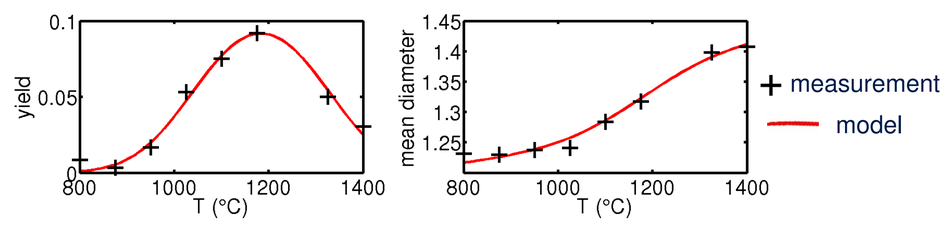
- n(d) : nucleation window = rectangular function
- s(d) : catalyst particle diameter distribution
  = Gaussian distribution
- g(d) = n(d) • s(d) : growth function

T = temperature
C = composition of catalysts

- yield: $N_{CNT}(T,C) = \int_{-\infty}^{\infty} g(d^{CNT},T,C)\delta d^{CNT}$
- mean diameter: $d_0^{CNT}(T,C) = \frac{1}{N_{CNT}} \int_{-\infty}^{\infty} d^{CNT} g(d^{CNT},T,C)\delta d^{CNT}$
- assumptions: $d^{CNT} = d^{CP}$: catalyst particle diameter = CNT diameter
  $d_0^S(T) = a + bT$: position of s(d) shifts linearly with T
- model parameters: σ^s = spread (standard deviation) of s(d)
  N^{cp} = area below s(d) = number of catalyst particles
  d_{min} ,d_{max} = boundaries of n(d)
  a, b = parameters of $d_0^S(T) = a + bT$

Results: Fit of the CVSA Model to Measured Data

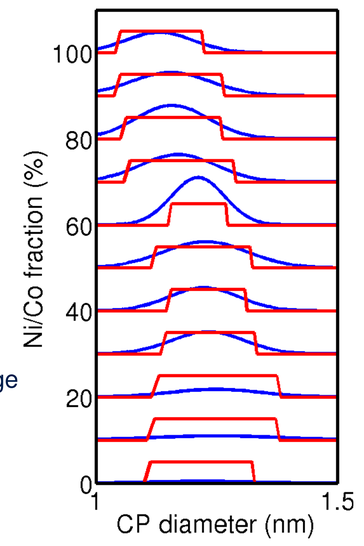
High yield catalyst mix **Ni:Co:Mo = 5:4:1**



model parameters: σ^s = 0.100 nm ∓ 13.6%
N^{cp} = 0.108 a.u. ∓ 11.9%
d_{min} = 1.18 nm ∓ 1.3%, d_{max} = 1.47 mn ∓ 1.3%
a = 0.143 nm ∓ 9.4%, b = 0.001 nm/°C (fixed)

Catalyst mix with **different Ni:Co fractions** [1]:

- Results: with increasing Ni:Co fraction
  - the position of n(d) shifts towards smaller diameters
  - the spread of s(d), σ^s, changes very little
  - the number of catalyst particles, N^{cp}, changes strongly
- Problems:
  - fitting procedure needs to have the maximum of the yield in the measured range
  - some model parameters are correlated
  - measurements at low yields are very noisy = very hard to fit



Outlook

- more measurements are necessary to improve the data density
- unbiased data processing for OAS spectra needed
- improve the model and the fitting procedure
  (resolve correlated parameters and maximum yield problem)
- test reliability of model parameters to allow for a physical interpretation
- interplay of model and mesurements to improve our understanding of the CNT growth mechanism

References

[1] S. Tetali *et al.*, “Unravelling the Mechanisms Behind Mixed Catalysts for the High Yield Production of Single-Walled Carbon Nanotubes”, ACS Nano **3**, 3839 (2009).
[2] M. H. Rümmeli *et al.*, “Catalyst Volume to Surface Area Constraints for Nucleating Carbon Nanotubes”, J. Phys. Chem. B **111**, 8234 (2007).