Mapping the carbon nanotube formation parameter space: Data mining and mechanistic understanding for efficient resource use

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2017 SNO Conference
CNTs in Spotlight

Booming interests

Widespread applications

Composite

Aligned CNTs

Fabric & Interconnects

Nanodevice

Environmental Energy

Image Courtesy of De Volder Group at Cambridge

De Volder et al. Science, 2013
Delayed Environmental Investigation

Topic: “carbon nanotube”

(a)

(b)

Topic: “carbon nanotube” AND “environmental impact”

ISI Web of Science database
partial data for 2016

Shi et al. Green Chemistry, 2017
Sustainable CNT Production Challenges: Energy and Resources

Chemical Process

Operating system

Heterogeneous catalytic interface

Tube furnace
Address Challenges: Looking Backward

Backward:
- universal mechanistic insights might exist inside widespread recipe formulations
- inform green synthesis design

Forward: manufacturing innovations
- More efficient precursor
  Alkynes growth
- More sustainable resources
  Gaseous product mixture from Fischer-Tropsch synthesis
  Upcycling waste plastics
  Electrochemical conversion of CO₂
- Reactor modifications
  Continuous manufacturing
  Gas flow direction control
  Cold-walled reactor
Data Extraction

**Chosen groups**

Topic: “carbon nanotube” AND “growth” AND “chemical vapor deposition”

Searched results: 2744

**Collected parameters**

Energy
- Temperature

Resource
- $C_xH_y$ source
- $C_xH_y$ flow rate
- $H_2$ flow rate
- Carrier gas type
- Carrier gas flow rate
- Enhancer type
- Enhancer concentration
- Catalyst

Other
- Reactor type
- Reactor size

ISI Web of Science database
Pattern 1: Temperature Dependence
Clarify Potential Biases: Experiments

![Graph showing mass yield vs. temperature with different gas mixtures]
Implication of Temperature Decrease

Thermal Loss Model

Energy saving: $1.3 \times 10^{11}$ J/kg CNTs
Annual production: $2.2 \times 10^6$ kg/year

$=2.9 \times 10^{17}$ J/year ~ 7 million US household electricity consumption

Shi et al. Green Chemistry, 2017
Pattern 2: 
Material Demand: C and H loading

CH₄: high C loading

C₂H₂: low C loading

Shi et al. Green Chemistry, 2017
Varied $\text{H}_2$ dependence

![Graphs showing proportion of $\text{H}_2/C_{x}H_{y}$ for different compounds: $\text{CH}_4$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_2$.](image)

Shi et al. Green Chemistry, 2017
Role of H$_2$

**Enhanced yield**

- 10% C$_2$H$_4$
- 10% C$_2$H$_4$ + 10% H$_2$

**Improved quality**

- 10% C$_2$H$_4$ @ 800 °C
- 10% C$_2$H$_4$ + 10% H$_2$ @ 800 °C

**Diameter tuning**

- 10% C$_2$H$_4$
- 10% C$_2$H$_4$ + 10% H$_2$

Enhanced yield:
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# Atom Carbon Efficiency

$$\text{Atomic Efficiency} = \frac{\text{C mass in CNT}}{\text{C mass in input precursor}}$$

<table>
<thead>
<tr>
<th>Growth Condition</th>
<th>Atomic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Futaba et al. (Hata Group, 10% C\textsubscript{2}H\textsubscript{4}, 750 °C)</td>
<td>0.042%</td>
</tr>
<tr>
<td>Li et al. (Hart Group, 17% C\textsubscript{2}H\textsubscript{4}, 775 °C)</td>
<td>0.050%</td>
</tr>
<tr>
<td>Plata et al. (20% C\textsubscript{2}H\textsubscript{4}, 725 °C, cold-wall reactor)</td>
<td>0.002%</td>
</tr>
<tr>
<td>Plata et al. (Alkyne-assisted 20% C\textsubscript{2}H\textsubscript{4}, 725 °C, cold-wall reactor)</td>
<td>0.026%</td>
</tr>
<tr>
<td>10% C\textsubscript{2}H\textsubscript{4}, 800 °C</td>
<td>0.038%</td>
</tr>
<tr>
<td>10% C\textsubscript{2}H\textsubscript{4} + 10% H\textsubscript{2}, 800 °C</td>
<td>0.061%</td>
</tr>
<tr>
<td>1% C\textsubscript{2}H\textsubscript{2}, 800 °C</td>
<td>0.42%</td>
</tr>
</tbody>
</table>

Shi et al. Green Chemistry, 2017
Mechanistic Insights
Future Work

➢ Should be automated for high-throughput screening

➢ Methodology transferable to green synthesis of other novel materials

➢ Link product application performance to synthetic methodologies

Image courtesy of Kong group at MIT
Temperature evolution

(a) 750 °C
(b) 800 °C
(c) 850 °C
(d) 900 °C
(e) 950 °C
(f) 1000 °C