Synthesis of Metal Nanoparticle-Decorated Carbon Nanotubes under Ambient Conditions

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Preparation of Metal Nanoparticle-Decorated CNTs

- Metal nanoparticles + CNT
- Electrochemical methods
- Electroless methods
  - Sputtering
  - Activation bath
  - Use of reducing agents
    - Solid-phase reduction
    - $H_2$
    - Dispersion in solvents
      - NaBH$_4$
      - Ethylene Glycol
  - Pyrolysis from organometallic compounds
  - Spontaneous reduction
  - Substrate-Enhanced Electroless Deposition (SEED)
Thermal Decomposition of Metal Acetates in the Presence of CNTs

- Electroless
- Solventless
- No added reducing agent
- Readily scaled-up

\[
\text{CH}_3\text{COOAg} \rightarrow \text{Ag} + \text{CH}_3\text{COOH} + C + \text{CO}_2
\]

To Improve from Mortar/Pestle Mixing

- SPEX CertiPrep 8000D *High-Energy Shaker Mill*
  - ~1000 cycles/min
  - 2.25” back and forth and 1” side-to-side movements
  - Zirconia vial: ~20 mL mixing load
  - Two zirconia balls: d ~0.5”
Thermal Decomposition of Metal Acetates in the Presence of CNTs

\[ \text{CH}_3\text{COOAg} \rightarrow \text{Ag} + \text{CH}_3\text{COOH} + \text{C} + \text{CO}_2 \]

- 1 mol% AgOAc (to C)
- 2-min Milling
- 350 °C N₂ 3h

2-min Milling without Thermal Treatment
Sintering or Intermediate?

S-5200 5.0kV -0.3mm x 150k SE

Sintering or Intermediate?

150 °C N₂

AgOAc

Ag
1. Formation of \( \text{AgOAc} \) nanoparticles
2. Decomposition of \( \text{AgOAc} \) on C surface

Sintering or Intermediate?

2-min Milling *without* Thermal Treatment
10-min Milling without Thermal Treatment

Formation of Ag (0) Nanoparticles on MWNT Surface
Estimated Yield of Conversion

1 mol% AgOAc Feed (10-min Milling): ~40-60%

Estimation from Thermal Decomposition (350°C)

Shorter Milling, Less Conversion

1 mol% AgOAc Feed (2-min Milling): ~10-20%

Estimation from Thermal Decomposition
Conversion vs. Milling Time

<table>
<thead>
<tr>
<th>Ball-Mill Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>120-min</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>10-min</td>
<td>40-60%</td>
</tr>
<tr>
<td>2-min</td>
<td>10-20%</td>
</tr>
</tbody>
</table>

- 1% AgOAc Feed

Can’t Mill Too Long

- 30-min
- 60-min
- 120-min
Dependence on CNT Diameter?

- 1% AgOAc Feed
- ~10 min Milling

CNT Diameter

Expanded Graphite
- 60-100 nm
- 40-60 nm
- 10-30 nm
- 3-8 nm
- SWNT

- 3-8 nm
- 10-30 nm
- 60-100 nm

EG

- 10mol% AgOAc Feed
- 10-min Milling
Yield of Conversion

1 mol% AgOAc Feed (10-min Milling): ~40-60%

More Ag Feed, Less Conversion

10 mol% AgOAc Feed (10-min Milling): ~5-10%

Estimation from Thermal Decomposition
More Ag, More Decoration

10 mol% AgOAc feed; 10-min milling
Similar average size ~2.5 nm
Other Metals?

- Fe(OAc)$_2$
- Cu(OAc)$_2$
- H$_2$Pt(OH)$_6$
- PtOAc

- 1 mol% feed
- 10-min milling
Pd(OAc)_2

T_{dec} \sim 205^\circ C

Pd Nanoparticle-Decorated MWNTs

- Homogeneous Decoration of sub-2nm Pd(0) nanoparticles
- Exhibit excellent catalytic properties
Pd Nanoparticle-Decorated MWNTs

Conclusions

• **Advantages**
  – Ambient conditions
  – Electroless, solventless, no reducing agent
  – Rapid, single-step (< 30 min), readily scaled up
  – Narrow size distribution (sub-5 nm)
  – Widely applicable to various carbon substrates
  – Applicable to various metals: Ag, Pd, Pt ...

• **Limitations**
  – Conversion at the expense of nanotube structural integrity
  – Not universal to all metal salts?

• **Applications**
  – **Catalysts** at the expense of nanotube structural integrity
  – Sensitive
  – Electromagnetic devices
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