Nanoscopic Metal Oxide Objects \textit{via} Controlled Creation and Rearrangement of Amorphous Nanoparticles

Sankar Nair

School of Chemical & Biomolecular Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0100

December 11, 2007
Assembly of Nanoscopic Metal Oxide Objects

- Metal oxides offer a vast range of technologically interesting properties: catalytic, transport, mechanical, electronic, optical.

- Shrinking them into nanoscopic objects (nanotubes, nanoshells) offers exciting prospects for new nanotechnological materials and nanoscale devices.

- Metal oxide assembly in aqueous phase can be controlled by a variety of handles: temperature, pH, electrolytes.

- Can single-walled metal oxide nanotube objects be assembled from precursors?

- Can the shape, size, curvature, composition be controlled?

- What are the chemical/physical limits of such engineering?

- Existence of a unique model system to study these issues: precursor to a possible generalized strategy for metal oxide nanotube engineering?
Aluminogermanate (Al-Ge) Nanotubes

- Hydrophilic aluminum hydroxide shell
- Pendant germanol groups
- Exclusively single walled nanotubes with precise outer and inner diameters
- Average length ~ 20 nm*

* Mukherjee et al, Chemistry of Materials (2005)
Aluminogermanate (Al-Ge) Nanotubes

- Ordered single-walled nanotube materials by aqueous-phase synthesis
- Early evidence of non-conventional growth mechanism

Mukherjee et al, Chemistry of Materials (2005)
Aluminogermanate Nanotube Synthesis Process

Step 1 - Hydrolysis

- 5 mM AlCl₃ Solution in Water

Step 2 - Basification

- 0.1 N NaOH
  - pH 5.0

Step 3 - Acidification

- 0.1 M HCl & 0.2 M AcOH
  - pH 4.5

Step 4 - Equilibration

- 1.0 hr Equilibration
  - 0.1 M HCl & 0.2 M AcOH

Step 5 - Reaction

- 3.0 hr Equilibration
  - Reaction at 65-95°C under reflux conditions

- Importance of Steps 1-4
  - Chemical environment of synthesis solution
  - Characterization of evolving colloid at each step
Chemical Environment of Precursors in Steps 1-4

- Step 1 (hydrolysis) product is significantly different from all other products.

- Chemically, the products of Step 2, 3 & 4 are similar to that of the final nanotube i.e., Al-O-Ge bonds have been established.

Nanoparticle Evolution - Dynamic Light Scattering

- pH control (basification) condenses precursors to form oligomers with Al-O-Ge bonds
- Re-acidification prevents precipitation of amorphous materials
• At 95°C and 85°C average nanoparticle size increases slowly
• Even though no nanotubes are detected in 65°C and 75°C, nanoparticles are present
• DLS intensity normalized by particle size is a measure of concentration

• Nanoparticle concentration increases by almost two orders of magnitude when nanotubes are formed
The precursors first condense into Amorphous NanoParticles (ANPs).

The ANPs rearrange into ordered NanoTubes (NTs).

A simple model was developed that assumes:
- A quasi steady-state for the amorphous nanoparticles \( dC_{ANP}/dt \sim 0 \)
- The concentrations of nanotubes changes, dimensions remain constant

Quantitative Kinetic Model - Solution

\[ C_{NT} = \text{Concentration of nanotube} \quad C_{ANP} = \text{Concentration of amorphous nanoparticles} \]

\[
\frac{dC_P}{dt} = -k_1 C_P + k_{-1} C_{ANP}
\]

\[
\frac{dC_{ANP}}{dt} = \frac{k_1 C_P}{N_P} - \frac{k_{-1} C_{ANP}}{N_P} - k_2 C_{ANP} = 0 \quad (QSS)
\]

\[
\frac{dC_{NT}}{dt} = k_2 C_{ANP}
\]

\[
C_{P}(t) = C_P^0 e^{-Kt}
\]

\[
C_{ANP}(t) = \frac{C_P^0 K}{k_2 N_P} e^{-Kt}
\]

\[
C_{NT}(t) = \frac{C_P^0}{N_P} \left[ 1 - e^{-Kt} \right]
\]

\[
K = \frac{k_1 k_2}{k_{-1} + k_2} \quad \text{Overall effective NT formation rate constant}
\]
Average particle size in DLS is due to both ANPs and NTs

\[ L_{DLS} = \frac{L_{ANP} C_{ANP} + L_{NT} C_{NT}}{C_{ANP} + C_{NT}} \]

- \( L_{ANP} = 5.9 \) nm
- \( L_{NT} = 17.6 \) nm

\[ C_{ANP}(t) = \frac{C_{P0} K}{k_2 N_P} e^{-K t} \]
\[ C_{NT}(t) = \frac{C_{P0}}{N_P} \left[ 1 - e^{-K t} \right] \]

- Increase in average particle size is due to the ANP \( \rightarrow \) NT transformation
Effects of Composition (Si/Ge ratio)

Progressive substitution of Ge with Si allows a series of Al-Ge-Si nanotubes

What is the effect of Si/Ge ratio on the mechanism of AlSiGe nanotube formation in the framework of the ANP → NT mechanism?

Length Control

- Length increases from ~20 nm in Al-Ge to ~100 nm in Al-Si nanotubes

Diameter Control

- Diameter decreases from 3.4 nm in Al-Ge to 2.2 nm in Al-Si nanotubes
Composition of Nanotubes - XPS and FTIR Analysis

- Ge content in the final product follows closely the precursor composition
- Ge content can be reproducibly varied and measured
The Amorphous Nanoparticle size is dependent on the Si/Ge ratio.
Both ANPs and NTs show the same trend of decreasing size as Ge content increases.
Extrapolation of ANP Size from NT Length

AlGe Nanotube

5.87 nm  ➔  17.6 nm

14.3 Al atoms/nm³

Al-Si-Ge Nanotube with 10% Ge

x nm  ➔  91 nm

x = 10.1 nm

• These extrapolated NT lengths are close to the fitted size of the ANPs
Preliminary Proposal for Composition Effects on Al-Ge-Si Nanotube Length

• Analysis within the framework of our ANP \(\rightarrow\) NT mechanistic model
  • Model is supported by detailed studies on Al-Ge nanotubes
  • Tracking of average nanoparticle size by DLS as a function of time and temperature
  • Extraction of NT and ANP sizes using appropriate models of nanoparticle diffusion (rigid rods and spheres)

• Extension of DLS methods to Al-Si-Ge nanotubes
  • ANP diameter and resulting NT length follow the same trends
  • Evidence for strong correlation between these nanoparticle sizes

• Preliminary proposal: As Ge content decreases, the initial condensation process generates larger ANPs which hence transform to larger NTs

• This ‘first order’ model is being developed in more detail – DOSY NMR spectroscopy, optical (IR/Raman/UV-Vis) spectroscopy
Energetics of Carbon Nanotubes

- Graphite is the most stable carbon sp\(^2\) structure
  
  No energy minimum with diameter → polydispersity in NT diameter

Is there a quantitative correlation between the composition, diameter, and internal energy of mixed-oxide aluminosilicogermanate NTs?
Methodology for Internal Energy Computations

- Force field Parameterization
- Force field validation via structural and vibrational data
- Initial NT model construction with varying Si/Ge composition
- Model structure optimization by energy minimization
- Energy equilibration and data production MD simulations

\[ E = \frac{e^2}{4\pi\varepsilon_0} \sum_{i\neq j} \frac{q_i q_j}{r_{ij}} + \sum_{i} E_{ij} \left[ \left( \frac{R_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{ij}}{r_{ij}} \right)^6 \right] + k_{ij} (r_{ij} - r_o)^2 \]

Optimized Lennard-Jones parameters for Ge using Na[AlGeO₄], K[AlGeO₄], α-GeO₂ crystal structures

- NT models constructed as isolated entities to avoid inter-tube interactions
- 3 D periodic boundary conditions

Steepest Descent, Conjugate Gradient methods

- NVT@ 298 K using CLAYFF force field*
- Simulation time step used - 0.9 fs
- Berendsen thermostat

Energy minimum $\rightarrow$ monodispersity in SWNT diameter

- Energy minima shift progressively to higher diameters with increasing Ge content

Radial Breathing Mode of Single–Walled NT

- Radial breathing mode (RBM) frequency sensitive to NT diameter
  - Obeys inverse power law dependence on the radius
  - Pre-exponential constant decreases with increase in Ge content - consistent with vibrational frequency shifts in IR


Simulated RBM of AlSiGeOH NTs
‘Force-Constant’ Model of Nanotube Energetics

- Strain energy model to predict diameters of NT materials
  - E.g. Si substituted by Ge → AlGe NT or varying Si/Ge molar ratios → AlSiGeOH NT

Framework Oxides (e.g., Zeolites)
- 3-D Structures
- Can be modeled as totally ‘rigid’ SiO$_4$ units with flexible joints
- More than 200 different zeolite structures result from the “flat” energy landscape


Al-Ge-Si Nanotubes
- AlO$_6$ and SiO$_4$ are confined into a cylindrical geometry
- Changes in diameter must be accompanied by changes in Al-O and Si-O bond lengths
- Nanoscale confinement effects are important
Force-Constant Model of Nanotube Energetics

- Harmonic potentials to model the Al-O, Si-O, and Ge-O bond energies

\[ V_{\text{Al-O}} = K_1 (d_1 - d_{1e})^2, \quad V_{\text{Si-O}} = K_2 (d_2 - d_{2e})^2 \quad \text{and} \quad V_{\text{Ge-O}} = K_3 (d_3 - d_{3e})^2 \]

- Geometric relationships between the bond lengths and the number of Al atoms in the circumference

<table>
<thead>
<tr>
<th>Major axis of hexagon</th>
<th>Al-O bond length</th>
<th>Si-O/Ge-O bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{\text{Al-Al}} )</td>
<td>( d_1 \sqrt{6} )</td>
<td>( d_2 ) or ( d_3 = \frac{d_1}{\sqrt{2}} )</td>
</tr>
</tbody>
</table>
Model Predictions and Fit to Simulation Data

Internal Energy \( \bar{E}(N) = \bar{E}_0 + \frac{2}{7} K_1 (d_1 - d_{1e})^2 + \frac{3}{14} [xK_2 (d_2 - d_{2e})^2 + (1-x)K_3 (d_3 - d_{3e})^2] \)

RBM frequency \( \omega_{RBM} = 2\pi f_{RBM} = \sqrt{4N(4K_1 + 1.5[xK_2 + (1-x)K_3])/3M \sin(2\pi / N)} \)

- Fit results:
  - \( d_{1e} = 0.197 \) nm, \( d_{2e} = 0.159 \) nm, \( d_{3e} = 0.173 \) nm
  - Strain energy and RBM frequency well reproduced by the model!
Correlation between NT Composition, Diameter and Internal Energy

- Difference in Si-O/Ge-O and Al-O bond energies induces a strain energy minimum
  - Ge-O strain potential energy is higher than Si-O
    - Energy minimum in AlGeOH NT occurs at larger diameter

- Experimental estimation of the NT diameter
- Quantitative correlation between predicted shift in outer NT diameters and composition estimated via XRD
  - First intense peak shifts towards lower 2θ regions with increase in Ge content
  - Indicates that inter-nanotube spacing is increasing
Comparison of Experimental and Predicted NT Diameters

- Experimental trends are correctly predicted
  - Quantitative deviations partly due to semi-quantitative relation between XRD peak location and NT diameter

Nanotube diameters from XRD data

• Al-Ge-Si-OH single-walled nanotubes: unique nanoscopic objects!

• Growth mechanism is quite different from the “nucleation-growth” paradigm existing for nanotube materials

• An “amorphous condensation + internal rearrangement” mechanism

• There are significant effects of composition on the dimensions (length and diameter)

• Nanotube length can be influenced by controlling the amount of material condensed in the amorphous nanoparticles (ANPs), which in turn can be controlled by varying the Si/Ge ratio

• Diameter appears to be controlled by internal energy considerations – the existence of a unique energy minimum in the nanotube diameter has been established

• Insights to develop synthesis routes based on “amorphous condensation + self assembly” for ordered metal oxide nanoscopic objects of very small dimensions and complex internal structures