In Quest of a Systematic Framework For Unifying and Defining Nanoscience

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The Concept

A systematic framework is proposed for unifying and defining nanoscience.

This systematic framework is based on the same “first principles” initiated by Lavoisier, Dalton, Mendeleev and others that led to a “periodic system and central paradigm” for traditional elemental atom and small molecule chemistry.
I. Introduction
Background and Historical
Brief Historical Overview

19th/20th Century Chemists/Physicists

- A. Lavoisier (1789)
- J. Dalton (1808)
- R. Feynman (1959)

Alchemy

Pre-1789

D. Mendeleev (1869)

Atom Periodicity

Nano-Alchemy (1959-Present)

Nanostructures
Assemblies

Molecular Structures

Atoms

PICOMETER

10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12}
First Systematic, Synthetic Nanostructure Platform

Dendrimers (early 1980s)

DNA
Lipid Bilayer

Proteins

decimeter (dm)
tens

centimeter (cm)
hundreds

millimeter (mm)
thousands

micrometer (μm)
millions

nanometer (nm)
billions

picometer
trillions

Dendrimers
Core G=0 G=1 G=2 G=3 G=4 G=5 G=6 G=7

Nanoscale Building Blocks

Dendrimers Quantum Dots Fullerenes Nanotubes

Small Molecules

Atoms
Traditional Chemistry – “Central Dogma”
First Principles

- Atoms Form Chemical Bonds
- Atoms Bond with Discrete Stoichiometries, Valency and Combining Weights
- Atoms Bond with Discrete Directionality
- Atoms Exhibit Periodic Properties

John Dalton (1808)

Atoms

Compound Atoms
Atom Mimicry:

(a) Core-Shell Architecture
(b) Outer Shell Reactivity
### Picoscale Matter (Atoms)

<table>
<thead>
<tr>
<th>Elements Exhibiting Noble Gas Configurations</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron shell levels</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Diameters</td>
<td>.064 nm</td>
<td>.138 nm</td>
<td>.194 nm</td>
<td>.220 nm</td>
<td>.260 nm</td>
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<tr>
<td>Saturation values (n)</td>
<td>2</td>
<td>10</td>
<td>18</td>
<td>36</td>
<td>54</td>
</tr>
<tr>
<td>Atomic weights</td>
<td>4.00</td>
<td>20.17</td>
<td>39.94</td>
<td>83.80</td>
<td>131.30</td>
</tr>
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</table>

### Hard Nano-Matter (Gold Nanoclusters)

<table>
<thead>
<tr>
<th>Atom shell levels</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>Diameters</td>
<td>.864 nm</td>
<td>1.44 nm</td>
<td>2.02 nm</td>
<td>2.59 nm</td>
<td>3.17 nm</td>
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<tr>
<td>Saturation values (n)</td>
<td>12</td>
<td>54</td>
<td>146</td>
<td>308</td>
<td>560</td>
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<tr>
<td>Nano-cluster weights</td>
<td>2560</td>
<td>10833</td>
<td>28953</td>
<td>60861</td>
<td>110495</td>
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</table>

### Soft Nano-Matter (Dendrimers)

<table>
<thead>
<tr>
<th>Monomer shell levels</th>
<th>G=1</th>
<th>G=2</th>
<th>G=3</th>
<th>G=4</th>
<th>G=5</th>
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<tbody>
<tr>
<td>Diameters</td>
<td>1.58 nm</td>
<td>2.2 nm</td>
<td>3.10 nm</td>
<td>4.0 nm</td>
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<tr>
<td>Saturation values (n)</td>
<td>9</td>
<td>21</td>
<td>45</td>
<td>93</td>
<td>189</td>
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<tr>
<td>Nanostructure weights</td>
<td>144</td>
<td>2414</td>
<td>5154</td>
<td>10632</td>
<td>21591</td>
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</tbody>
</table>

---

**Comparison of Atoms with Hard and Soft Nanoparticles**

Self-Assembly of PAMAM Dendrimers (G9) (Atom Mimicry)

Spheroidal Valency Defined by Nano-Sterics

<table>
<thead>
<tr>
<th>Dendrimer Symmetry</th>
<th>N_{max}</th>
<th>( \frac{r_1}{r_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal, D₃h</td>
<td>2</td>
<td>0.155</td>
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<tr>
<td>Tetrahedral, T₄</td>
<td>3</td>
<td>0.225</td>
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<td>Octahedral, O₆</td>
<td>6</td>
<td>0.414</td>
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<td>low symmetry</td>
<td>7</td>
<td>0.591</td>
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<tr>
<td>Square Antiprism, D₄d</td>
<td>8</td>
<td>0.645</td>
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<td>9</td>
<td>0.742</td>
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<tr>
<td>low symmetry</td>
<td>10</td>
<td>0.848</td>
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<tr>
<td>Icosahedral, I₆</td>
<td>12</td>
<td>0.902</td>
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<td>low symmetry</td>
<td>13</td>
<td>1.12</td>
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<tr>
<td>low symmetry</td>
<td></td>
<td>1.20</td>
</tr>
</tbody>
</table>

\( r_1 \) = radius of core dendrimer
\( r_2 \) = radius of shell dendrimer

Mansfield-Tomalia-Rakesh Equation

\[
N_{max} = \frac{2\pi}{\sqrt{3}} \left( \frac{r_1}{r_2} + 1 \right)^2
\]

When: \( \frac{r_1}{r_2} > 1.20 \)

Nano-Element Valency: \([H-1] \text{ type; } [\text{Cubic-(Ag)}_n]\)

\[
[\text{Metals}]^0 = \text{H}_2, \text{Cl}_2, \text{O}_2
\]

\[-(\text{CH}_2)_n = 3,4 = 2\text{-D Assembly}\]

\[
\text{CH}_4 = 3\text{-D Assembly}
\]

M. Rycenga, J. M. McLellan, Y. Xia; Adv. Mater.,(2008), 20, 2416-2420
Critical Hierarchical Design Parameters

Conservation of Hierarchical Design Parameters? (Atom → Molecular → Nano Structures)

Atom Mimicry

Architecture (Symmetry)
- Size
- Shape
- Surface Chemistry
- Flexibility

Nanostructures Assemblies
(CNDP)
Molecular Structures
(CMDP)
Atoms
(CADP)

Atom Periodicity
Conservation of Hierarchical Design Parameters?
(CADP → CMDP → CNDP)
Rudimentary Atomic Element Property Patterns Observed before Mendeleev

Physical Properties:

• Dependent on element mass (i.e., At. wt.)

Chemical Properties:

• Dependent on element valency
Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter**

By Donald A. Tomalia,* Adel M. Naylor, and William A. Goddard III
Critical Hierarchical Design Parameters

Atom Mimicry

Macroscale

Nano-Periodicity

Soft Nanoparticle Categories

Hard Nanoparticle Categories

Nano-elements

Nano-compounds

Nanoscale

Picoscale

Nanoscale

Architectures (Symmetry)

Size

Shape

Surface Chemistry

Flexibility

Nanostructures Assemblies (CNDP)

Molecular Structures (CMDP)

Atoms (CADP)
II. Proposed Nanomaterials Classification Roadmap
Nano-Element (Module) Categories (Selection Criteria)

1. Exhibit Well-Defined Monodispersity:
   (>90% monodisperse as a function of size and/or mass)

2. Well-Defined Nanostructures, Assemblies or Particles that Mimic / Behave Like Atoms:
   (They react, assemble and exhibit controlled Critical Nanoscale Design Parameter (CNDP) properties as a unit.)

3. Exhibit Well-Defined Stoichiometries and Mass Combining Ratios

4. Exhibit Nano-Periodic Property Patterns
Monodispersity Criteria:
Atom-Like, 3-D Nano-cluster Super Lattices

>90% monodisperse gold nanoclusters required to obtain well defined X-ray patterns

### Periodic Table of the Elements

#### Hard Matter
- **Metals**
  - Alkaline earth metals
    - 1A
      - Na
      - Mg
    - Alkaline metals
      - K
      - Ca
      - Sc
      - Ti
      - V
      - Cr
      - Mn
      - Fe
      - Co
      - Ni
      - Cu
      - Zn
- Transition metals
  - Transition metals
    - Th
    - W
    - Re
    - Os
    - Ir
    - Pt
    - Au
- Noble gases
  - He
  - Ne
  - Ar
  - Kr
  - Xe

#### Soft Matter
- **Non-Metals**
  - Halogens
    - F
    - Cl
    - Br
    - I
  - Noble gases
    - Ne
    - Ar
    - Kr
    - Xe
  - **Dendrimers**
  - **Dendrons**
  - **Proteins**
  - **Viral Capsids**
  - **RNA/DNA**

#### Hard Particle Nano-Element Categories
- **Metal (M°)**
  - Nanoclusters
- **Metal Chalcogenide**
  - Nanocrystals
- **Metal Oxide**
  - Nanocrystals
- **Silica**
  - Nanoparticles
- **Fullerenes**
- **Carbon Nanotubes**

#### Soft Particle Nano-Element Categories
- **Dendrimers**
- **Nanoparticles**
- **Polymeric Micelles**
- **Proteins**
- **Viral Capsids**
- **RNA/DNA**
Nanomaterials Classification Roadmap

Atom-Based Structures/Assemblies
- Diameters: 1-100 nm
- Mass: $10^4$-$10^{16}$ daltons
- # of Atoms: $10^2$-$10^8$
- Topology: 0-D and 1-D

Category I
- Well-Defined Materials
  - Hard Nanoparticles
  - Nano-elements
  - Soft Nanoparticles

Category II
- Undefined Materials

Soft Nanoparticles
- Insulators
- Non-Metal Organic Structures

Hard Nanoparticles
- Conductors
- Semi-Condensors

Nano-elements
- Metal Clusters
- Metal Oxides
- Silica Nanoparticles
- Molecular Organic Nanoparticles

Nano-compounds
- Metal Particle Nano-compounds
- Soft/Mixed Particle Nano-compounds
- Soft Particle Nano-compounds

Nano-periodic Properties
- Physico-Chemical
  - Size
  - Shape
  - Surface Chemistry

- Interior Features
  - Flexibility/Polarizability
  - Architecture

- Functional/Applications
  - Photonic
  - Magnetic
  - Electronic


The National Dendrimer & Nanotechnology Center
# Soft Particle Nano-Element Categories

<table>
<thead>
<tr>
<th></th>
<th>Dendrimers</th>
<th>Nano-latexes</th>
<th>Polymeric Micelles</th>
<th>Proteins</th>
<th>Viral Capsids</th>
<th>RNA/DNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>S-1</td>
<td>S-2</td>
<td>S-3</td>
<td>S-4</td>
<td>S-5</td>
<td>S-6</td>
</tr>
</tbody>
</table>

## Synthetic Polymers (Dendritic Architecture)

<table>
<thead>
<tr>
<th>Molecular Size (nm)</th>
<th>100</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimers</td>
<td>Dendrons</td>
<td>Cova...</td>
<td>Core-Shell Tecto(dendrimers)</td>
</tr>
<tr>
<td>1.2</td>
<td>5.0</td>
<td>3.0</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

## Synthetic Polymers (Linear Architecture)

<table>
<thead>
<tr>
<th>Self-Assemblies</th>
<th>Co-polymeric Micelles</th>
<th>Covalent Assemblies</th>
<th>Linear Polymers (1°-Structures)</th>
<th>Monomers</th>
<th>Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEGylated Substrates</td>
<td>Amphiphilic</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

## Bio-Polymers (Linear Architecture)

<table>
<thead>
<tr>
<th>Bottom-up Assembly Strategies</th>
<th>Complexity</th>
<th>Viral Capsids</th>
<th>Quaternary (4°) Sequenced Structure</th>
<th>Tertiary (3°) Sequenced Structure</th>
<th>Globular Fibrous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Secondary (2°) Sequenced Structure (protein subunits)</td>
<td>Primary (1°) Sequenced Structure (polypeptides)</td>
<td>α-amino acids</td>
<td>atoms</td>
</tr>
</tbody>
</table>
Hard Particle Nano-Element Categories

Metal (M°) (Nanoclusters)
Metal (Chalcogenide) (Nanocrystals)
Metal Oxide (Nanocrystals)
Silica (Nanoparticles)
Fullerenes
Carbon Nanotubes

H-1  H-2  H-3  H-4  H-5  H-6

# Soft Nanoparticle Compounds

<table>
<thead>
<tr>
<th>Nano-Elements</th>
<th>Dendrimers Dendrons</th>
<th>Nano-latexes</th>
<th>Polymeric Micelles</th>
<th>Proteins</th>
<th>Viral Capsids</th>
<th>DNA/RNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimers Dendrons</td>
<td>S-1:S-1</td>
<td>S-2:S-1</td>
<td>S-3:S-1</td>
<td>S-4:S-1</td>
<td>S-5:S-1</td>
<td>S-6:S-1</td>
</tr>
<tr>
<td>Proteins</td>
<td>S-2:S-4</td>
<td>S-3:S-4</td>
<td>S-4:S-4</td>
<td>S-5:S-4</td>
<td>S-6:S-4</td>
<td></td>
</tr>
</tbody>
</table>

Dendrimer-Cluster Compounds
Tomalia, et al.

IgG-Dendrimer Compounds
(Stratus®)
Siemens
Germany

DNA-Dendrimer Compounds
(Superfect®)
Qiagen, Ger.

HIV-Virus-Dendrimer Compounds
(VivaGel®)
Starpharma, AU

Tobacco Mosaic Virus Compound
Viral Capsid-RNA [S-5:S-6] Core-Shell Type, Nano-Compound

Tobacco Mosaic Virus

Diameter: 18 nm
Length: 300 nm
Helical Symmetry

Nano-Compound Stoichiometry:
2130×Protein Subunits [S-5]; 1×ss-RNA [S-6]

Subunits: 158 amino acids

ss-RNA: 6400 nucleotide units

## Soft/Hard Nanoparticle Compounds

<table>
<thead>
<tr>
<th>Nano-Elements</th>
<th>Dendrimers</th>
<th>Nanolatexes</th>
<th>Cross-linked Polymeric Micelles</th>
<th>Proteins</th>
<th>Viruses</th>
<th>DNA/RNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal (M⁺) (Nanoclusters)</td>
<td>S-1:H-1</td>
<td>S-2:H-1</td>
<td>S-3:H-1</td>
<td>S-4:H-1</td>
<td>S-5:H-1</td>
<td>S-6:H-1</td>
</tr>
</tbody>
</table>

**References:**
- Tomalia et al., J. Luminescence (2005)
Barrel Shaped, SWNT:DNA-[H-6:S-6]; Core-Shell Type Nano-Compound Series

Core-Shell; [H-6:S-6] Type Nano-Compounds

Nano-Periodic Property Patterns for a Series of [H-6:S-6] Nano-Compounds


**Table 1 | DNA sequence versus SWNT chirality**

<table>
<thead>
<tr>
<th>Chirality (n,m)</th>
<th>Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9,1)</td>
<td>(TCC)<em>{10}, (TGA)</em>{10}, (CCA)_{10}</td>
</tr>
<tr>
<td>(8,3)</td>
<td>(TTA)<em>{4}TT, (TTA)</em>{3}TTGTT, (TTA)_{5}TT</td>
</tr>
<tr>
<td>(6,5)</td>
<td>(TAT)<em>{4}, (CGT)</em>{3}C</td>
</tr>
<tr>
<td>(7,5)</td>
<td>(ATT)<em>{4}, (ATT)</em>{4}AT</td>
</tr>
<tr>
<td>(10,2)</td>
<td>(TATT)_{2}TAT</td>
</tr>
<tr>
<td>(8,4)</td>
<td>(ATTT)_{3}</td>
</tr>
<tr>
<td>(9,4)</td>
<td>(GTC)<em>{2}GT, (CCG)</em>{4}</td>
</tr>
<tr>
<td>(7,6)</td>
<td>(GTT)<em>{3}G, (TGT)</em>{4}T</td>
</tr>
<tr>
<td>(8,6)</td>
<td>(GT)<em>{6}, (TATT)</em>{2}T, (TCG)<em>{10}, (GTC)</em>{3}, (TCG)<em>{2}TC, (TCG)</em>{2}TC, (GTC)_{2}</td>
</tr>
<tr>
<td>(9,5)</td>
<td>(TGTT)_{2}TG</td>
</tr>
<tr>
<td>(10,5)</td>
<td>(TTTA)_{3}T</td>
</tr>
<tr>
<td>(8,7)</td>
<td>(CCG)_{2}CC</td>
</tr>
</tbody>
</table>

DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.

**Optical Absorption Spectra versus SWNT (n,m) Chirality**
V. Nano-*(Periodic)* Property Trends
Using Traditional “First Principles”

Nanoscale Atom Mimicry

Nano-elements

Hard Nanoparticle Categories

Soft Nanoparticle Categories

HARD PARTICLE NANO-ELEMENT CATEGORIES
- Metal (M°) Nanoclusters
- Metal (Chalcogenide) Nanocrystals
- Metal Oxide Nanocrystals
- Silica Nanoparticles
- Fullerenes
- Carbon Nanotubes

SOFT PARTICLE NANO-ELEMENT CATEGORIES
- Dendrimers
- Dendrons
- Nano-latexes
- Polymeric Micelles
- Proteins
- Viral Capsids
- RNA/DNA

Nano-compounds

Nano-Periodic Property Patterns

Intrinsic Properties

Functional/Application Properties

Nano-Periodic Trends of [S-1]-Type Nano-Elements (Dendrons) (Size, Shape, Surface Chemistry Driven Self Assembly Patterns)


*First Demonstration of Quasi-Equivalence with Synthetic Nanostructures*
Percec’s Nano-Periodic Self-Assembly Table

<table>
<thead>
<tr>
<th>n</th>
<th>Bn</th>
<th>Pr</th>
<th>Bp</th>
<th>BpPr</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>CO₂Me</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>CH₂OH</td>
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<td>COOH</td>
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<td>2</td>
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<td>CO₂Me</td>
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<td>X</td>
<td>CO₂Me</td>
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<td>X</td>
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<tr>
<td></td>
<td>COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Tertiary) Supramolecular Dendrimer Assemblies

(Quaternary) Dendrimer Assemblies

The spirit of this perspective is not to disrupt any natural physico-chemical laws, but to encourage new and different thinking.

This is a works in progress! Much more remains to be done.

Donald A. Tomalia

The Future

Nano-Periodicity

Atoms (Elements) (Periodic Table)

Simple Compounds (HCl, H₂O, NH₃, CH₄)

Sub-nano Modules (Aliphatic, Aromatic)

Functional Groups (-CO₂H, -NH₂, -OH)

Complex Compounds (Palytoxin, C₆₀)

Nanoscale Modules (Proteins, DNA, RNA)

Bio-assemblies (Viruses, Ribosomes)

Complex Organisms (Humans)

Organisms (Plants, Animals)

Simple Organisms (Bacteria)

Biological Cells

Complexity Staircase

Soft Nanoparticle Categories

Dendrons

Proteins

Viruses

RNA/DNA

Nano-latexes

Polymeric Micelles

Soft Particle Nano-Element Categories

Nano-latency

Quantized Building Blocks

Hard/Soft Nano-Elements

Nanoscale Atom Mimicry

Hard Nanoparticle Categories

Nanoclusters

Chalcogenide Nanocrystals

Metal Oxide Nanocrystals

Silica Nanoparticles

Fullerenes

Carbon Nanotubes

Metal (M°) Nanoclusters

Metal (Chalcogenide) Nanocrystals

Metal Oxide Nanocrystals

Silica Nanoparticles

Dendrimers

Dendrons

Proteins

Viruses

Polypeptide Chemistry

Polymer Chemistry

Complex Compounds (Palytoxin, C₆₀)

Functional Groups (-CO₂H, -NH₂, -OH)

Sub-nano Modules (Aliphatic, Aromatic)

Simple Compounds (HCl, H₂O, NH₃, CH₄)

Atoms (Elements) (Periodic Table)

Monomers

Synthetic Nano-Chemistry

Metal (M°)

(Nanoclusters)

Metal (Chalcogenide)

(Nanocrystals)

Metal Oxide

(Nanocrystals)

Silica

(Nanoparticles)

Fullerenes

Hard Particle Nano-Element Categories

Carbon Nanotubes

Carbon Nanotubes

H₁ H₂ H₃ H₄ H₅ H₆
We are not advocating changes in the gospel! We are merely proposing some new hymns--new thinking.
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