SYNTHESIS OF ENERGETIC MATERIALS USING CARBON NANOSTRUCTURES

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The Next-Generation Converged Energy Materials Research Center (CEMRC)

- **Director:** Prof. Chang-Ha Lee  
  Yonsei University
- **Period:** 2012 – 2020
- **Research Group:** 11 Univ. & 1 Research Institute (34 doctors)
- **Budget:** about 10 mill. USD/9-yr

- Design and synthesis capability for the next-generation converged energetic materials
- Development of more powerful & less sensitive energetic materials
- Eco-friendly green technology for decayed energetic materials to valuable compounds
Technical Road Map of CEMRC

Design for Energetic Materials

Formulation

Multi-functional Energetic Particles

Demilitarization of Decayed Energetic Materials

Destruction, incineration, explosion, etc for decayed energetic materials → pollution, resource waste, safety issues

Today's Topic
Research on energetic materials focuses on

- Enhancing the power of its composites
- Increasing its insensitivity & stability
- Controlling the detonation properties

Mixing several chemicals to tune the explosive reactivity

**Potential benefits of nano-energetic materials:**

- More powerful
- More reliable & reproducible
- Safer to handle

*Higher density.*

*Controlled rate of energy release.*

*Reduced sensitivity.*
Nanomaterials : New platform for energetic materials

Advantages of Nanomaterials as new energetic materials
- Increased surface areas for higher density
- Enhancement of chemical reactivity by high thermal conductivity
- Ability to form composites with fuels by surface functionalization

Nanostructured Energetic Materials is a new concept composite powder, which can dramatically improve the performance of gunpowder and explosives
Single-Walled Carbon Nanotubes (SWNT)

Method of rolling graphene determines electronic property of SWNTs.

SWNTs can be either Metallic or Semiconducting.

Part I: Carbon Nanotube
Properties of Carbon Nanotubes

Mobility (cm²/V·s)
- CNT: 100,000
- Si: 1400
- GaAs: 8500

Current Density (A/cm²)
- CNT: 10⁹
- Al: 800
- Cu: 4020

Surface Area (m²/g)
- CNT: 1500
- Activated C: 500
- Silica: 800

Thermal Conductivity (W/m·K)
- CNT: 3500
- Silicon: 149
- Diamond: 2320

Ultimate Strength (GPa)
- CNT: 130
- C Fiber: 4
- Steel: 1

High Performance Transistor
- Display Solar Cell
- Interconnect
- Highly dense energetic materials
- Thermal conduits
- Propellant composites

Part I: Carbon Nanotube
Issues and Motivations

CNT guide thermal waves generated by the combustion of Cyclotrimethylene trinitramine (TNA) 
(Choi et al., Nature Mater. 9, p424, 2010)

The reaction velocity of TNA coated on CNT : 1,000~10,000 times faster than that of bulk TNA

- CNT with high thermal conductivity: Guide a chemically produced thermal wave

Technology Issues

Heterogeneities in the thickness of MWNTs as well as the TNA coated on the MWNT surface of MWNT/TNA composites

- Irregular performance along axial positions of the composites
- Performance controllability issue

Part I: Carbon Nanotube
Objectives

1. Achieve homogeneities of energetic materials-CNT composites (control issue)
   - CNT: Single-walled carbon nanotube (vs. multi-walled carbon nanotube)
   - Energetic materials: chemical attachment (vs. physical)

2. Increase combustion efficiency
   - CNT with high conductivity

Key factors investigated

We synthesized a series of nitrophenyl decorated CNT using diazonium chemistry

- explored CNT, with energetic materials, can release energy in a controllable manner
- investigate how thermal conductivity of CNT affects self-propagating explosive reactions

Part I: Carbon Nanotube
Electron transfer reaction between CNT – Diazonium

- Favored when oxidation potential of CNT > reduction potential of diazonium
- Nitrobenzene diazonium: highly reactive towards CNT
- Diazonium chemistry is efficient scheme to attach energetic molecule (Nitrobenzene) onto CNT surface homogeneously with high density
Covalent reaction scheme

**mono-nitrobenzene diazonium synthesis**

\[
\begin{align*}
O_2N-\equiv-NH_2 & \xrightarrow{\text{NOBF}_4} O_2N-\equiv-NBF_4^- \\
\text{Acetonitrile} & \text{N}_2, \text{-20°C} & \text{Stor}ed \text{ at -20°C} \\
\end{align*}
\]

Solid precipitate

**di-nitrobenzene attached CNT**

\[
\begin{align*}
\text{NH}_2-\equiv-\text{NO}_2 & \xrightarrow{\text{NOBF}_4} \text{N}^+\equiv\text{N}BF_4^- \\
\text{Acetonitrile} & \text{N}_2, \text{-20°C} & \text{Dissolved in H}_2\text{O} \\
\end{align*}
\]

**covalent reaction**

\[
\begin{align*}
\text{O}_2N-\equiv-NBF_4^- & \xrightarrow{\text{N}_2, \text{-20°C}} \text{O}_2N-\equiv-NBF_4^- \\
\text{SDS/H}_2\text{O} \quad \text{pH} = 5.5 & \text{45°C} \quad \text{Reacted} \\
\end{align*}
\]

Part I: Carbon Nanotube
Experimental

Energetic Materials Used

- HiPco SWNT (Hi-Pressure CO method): low thermal/electrical conductivity
- Arc SWNT (Arc Discharge method): high thermal/electrical conductivity

Physically mixed

Chemically bonded

Part I: Carbon Nanotube
Energetic materials-CNT composites formation

Reaction

Raman: D-band increases

UV-vis-nIR: absorption decays

Nitrophenyl groups (energetic materials) successfully attached to SWNT (monolayer deposition)

Part I: Carbon Nanotube
Chemical Attachment Effect

**Part I: Carbon Nanotube**

**Alone**
- Di-nitroaniline

**Physically mixed**
- Di-nitrobenezene + CNT mixture

**Chemically attached**
- Di-nitrobenezene functionalized CNT

**Temperature (°C)**
- **300.30 °C**  (Medium temperature)
- **373.60 °C**  (Broad range, High temperature)
- **280.33 °C**  (Narrow range, Lower temperature)

**Heat Flow (mW/g)**
- Melting
- Decomposition

**Graphs**
- Wt Corrected Heat Flow (mW/g) vs Temperature (°C)
Experimental

- Synthesis of silica nanoparticles as a template of nanoparticle.
  - Hard siNP
  - Porous siNP
  - siNP w/ ultralarge pore

- Synthesis of carbon nanoparticles
  - AlCl$_3$6H$_2$O was added to strengthen the silica nanoparticles
  - Phenol and Paraformaldehyde was added and heated for 36h to generate carbon nanoparticles.

Part II: Porous Carbon Nanoparticle
As a template for the porous carbon nanoparticle, we synthesized silica nanoparticles which possess multi-channel.

In order to load large amount of energetic materials, we made sphere silica nanoparticles inside, which will be removed and put out vacant volume as well as enlarge the pore diameter.
We coated the carbon materials on the silica nanoparticles. And it was confirmed that the structure of nanoparticles were maintained.

Future Work: we plan to remove the silica template in order to bring out the vacant volume to load energetic materials inside vacant space.
Conclusions

1. Homogeneous energetic materials-CNT composites were successfully formed using covalent chemistry.
2. Chemically bonded composites release energy at low temperatures over physically mixed ones.
3. Composites with highly conductive CNT show explosion at lower temperatures.
4. Synthesis of silica nanoparticles as a template was successfully fabricated.
5. For the better loading capacity, silica template of carbon nano particles are planned to be evacuated.
6. Enlarged cavity with carbon materials in carbon nanoparticles are expected to contribute better performances in loading and stabilizing large amount of energetic materials.
KISHEM-3 will be held in September, 2014: Yonsei University in Seoul, Korea
(More information: http://www.kishem.co.kr)

TOPICS
· Propellants
· High Explosives
· Insensitive Munitions
· Ageing
· Performance
· Synthesis
· Transformation of Decayed/Expired Materials
· Characterization
· Nano-Materials
· Improvements
· Manufacturing
· Detonation
· Physical Properties
· Theory

IMPORTANT DATES
· Due date for One-page Abstract: May 15, 2014
· Abstract Acceptance Notice: June 30, 2014
· Due date for Registration: July 31, 2014
· Session Schedule Notice: End of July, 2013
Thank you for your attention!

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