NDIA

2013 Insensitive Munitions & Energetic Materials Technology Symposium

SYNTHESIS OF ENERGETIC MATERIALS USING CARBON NANOSTRUCTURES

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Energy Materials Converged

국방과학연구소 AGENCY FOR DEFENSE DEVELOPMENT

방위사업청 Defense Acquisition Program Administration

국방기술품질원 DTaQ Defense Agency for Technology and Quality

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**

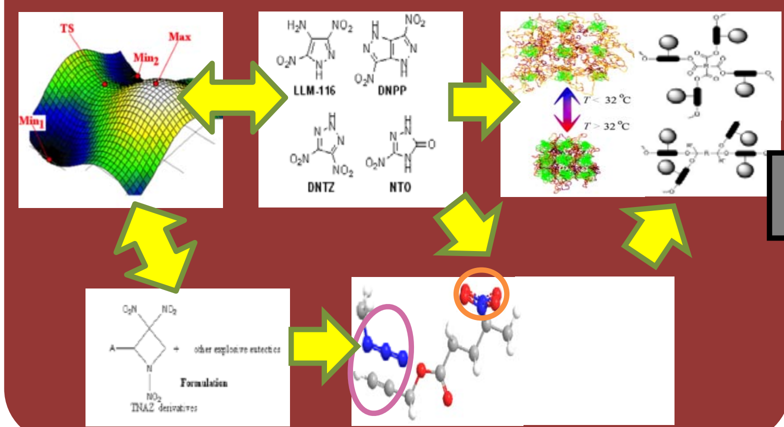
✓**Eco-friendly green technology for decayed energetic materials to valuable compounds**

Technical Road Map of CEMRC

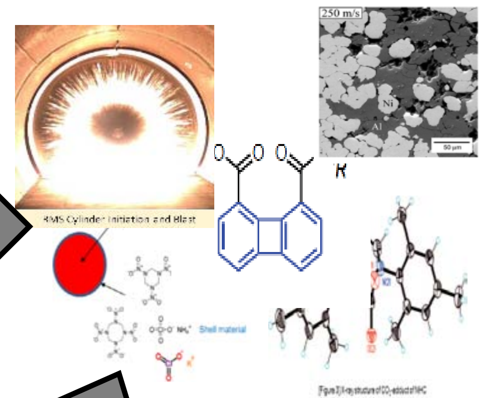
3

국방과학연구소
AGENCY FOR DEFENSE DEVELOPMENT

Design for Energetic Materials

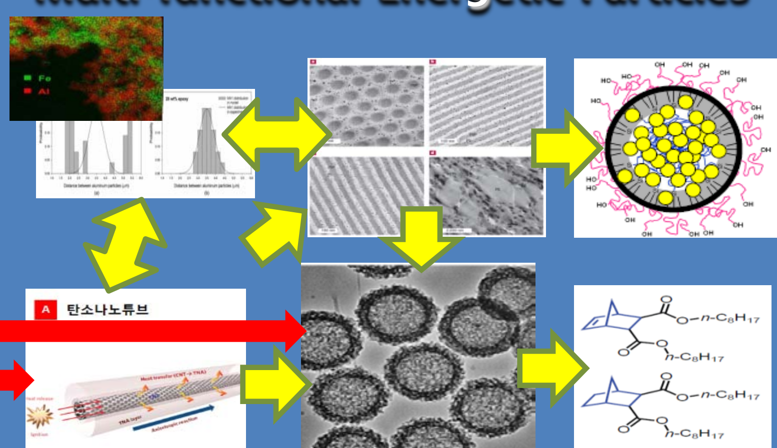


Formulation



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

Multi-functional Energetic Particles



Today's Topic

Demilitarization of Decayed Energetic Materials

Research on Energetic materials

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:

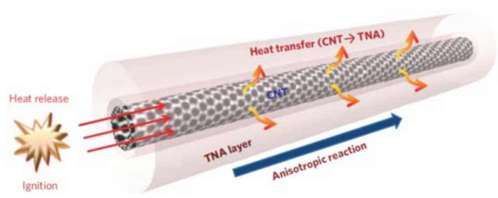
- •More powerful *Higher density.*
- •More reliable & reproducible *Controlled rate of energy release.*
- •Safer to handle *Reduced sensitivity.*

Nanomaterials : New platform for energetic materials

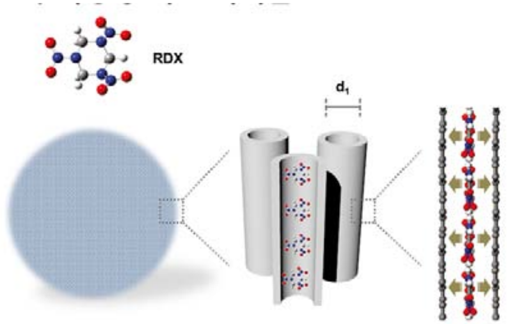
Nanomaterials

- **High Thermal Conductivity**
- **High Surface Area**
- **Stabilization**

Part I **A** **Carbon Nanotube**



B **Porous Carbon Nanoparticle** **Part II**



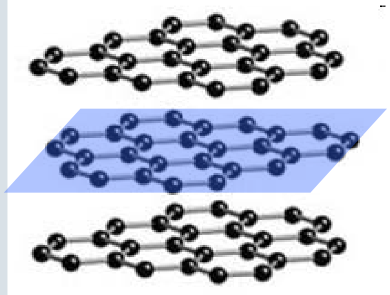
Advantages of Nanomaterials as new energetic materials

- Increased surface areas for higher density
- Enhancement of chemical reactivity by high thermal conductivity
- Ability to form composites with fuels by surface functionalization

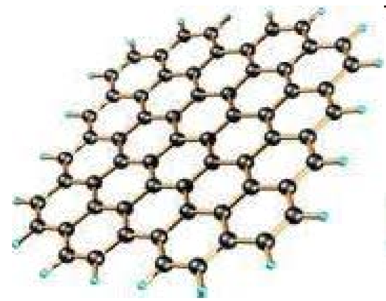
Nanostructured Energetic Materials is a new concept composite powder, which can dramatically improve the performance of gunpowder and explosives

Single-Walled Carbon Nanotubes (SWNT)

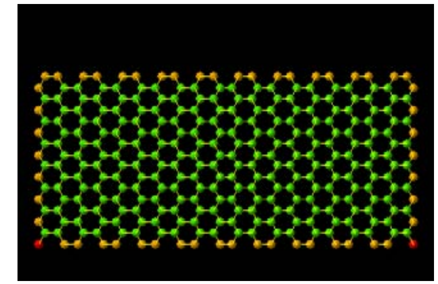
Graphite | **Graphene** | **Carbon Nanotubes**



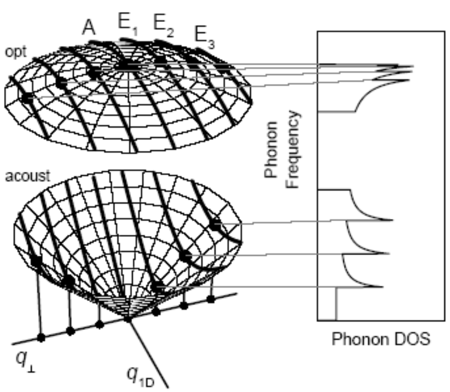
Extract layer



Fold layer

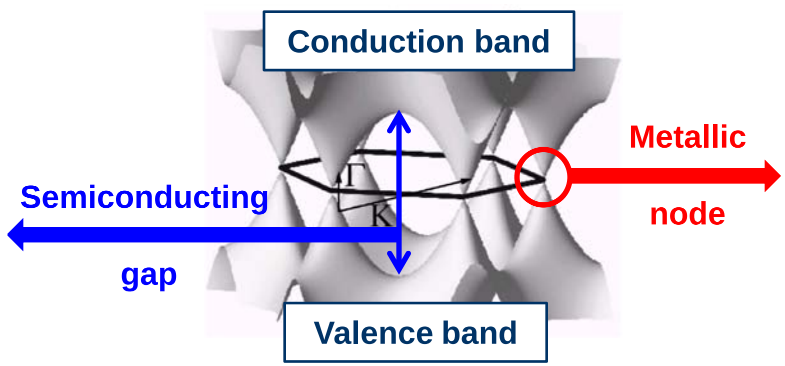


Method of rolling graphene determines electronic property of SWNTs



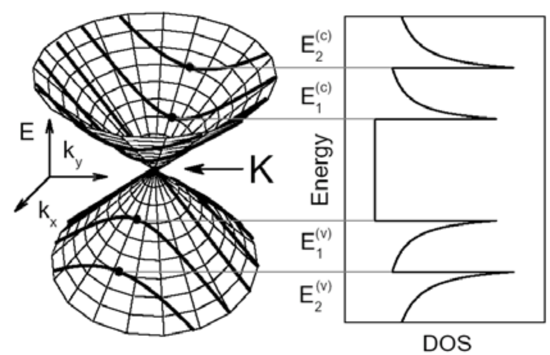
CNT electronic dispersion

(e.g. Semiconducting CNT)



Graphene electronic dispersion

(Zero-gap semiconductor)

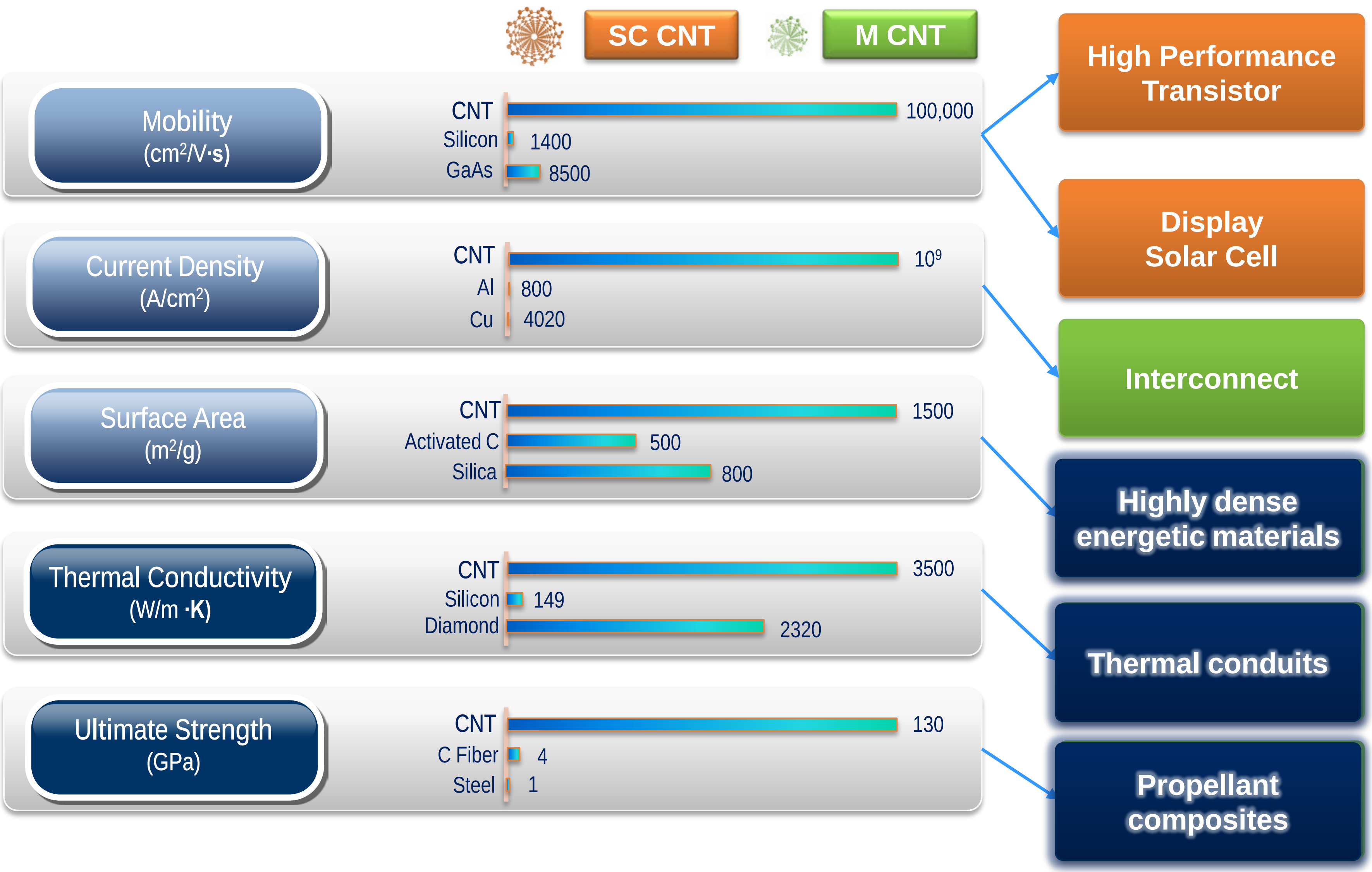


CNT electronic dispersion

(e.g. Metallic CNT)

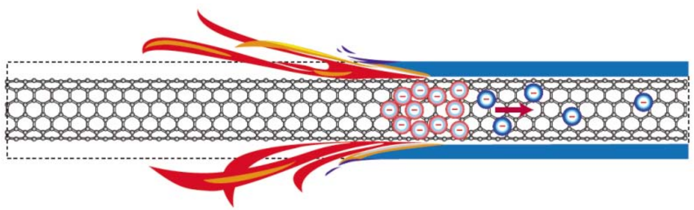
SWNTs can be either Metallic or Semiconducting

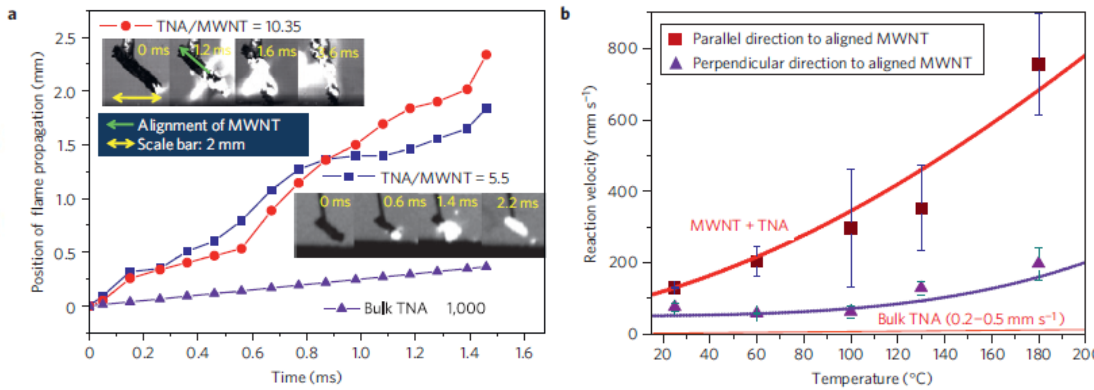
Properties of Carbon Nanotubes



Issues and Motivations

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





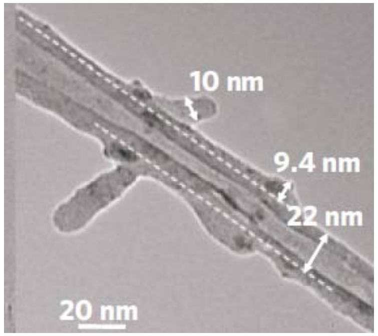
The reaction velocity of TNA coated on CNT : 1,000~10,000 times faster than that of bulk TNA
► CNT with high thermal conductivity: Guide a chemically produced thermal wave

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**



Objectives

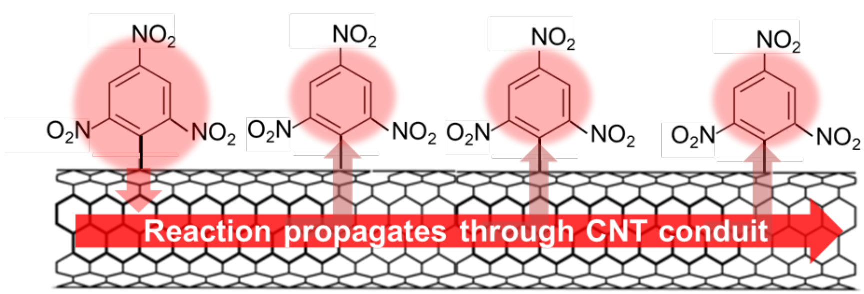
1. Achieve homogeneities of energetic materials-CNT composites (control issue)
   - CNT : Single-walled carbon nanotube (vs. multi-walled carbon nanotube)
   - Energetic materials : chemical attachment (vs. physical)
2. Increase combustion efficiency
   - CNT with high conductivity

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

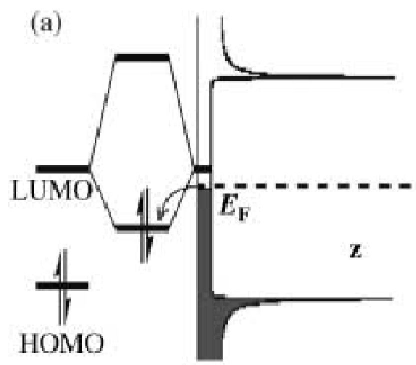


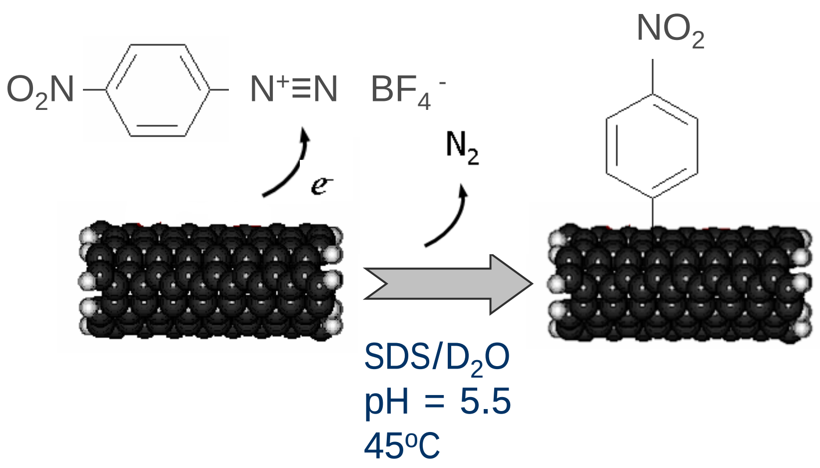
Diazonium chemistry: attach energetic materials on CNT

Chemical Potential of Diazonium-SWNT system

Reaction Scheme of Diazonium-SWNT system

Diazonium **SWNT**





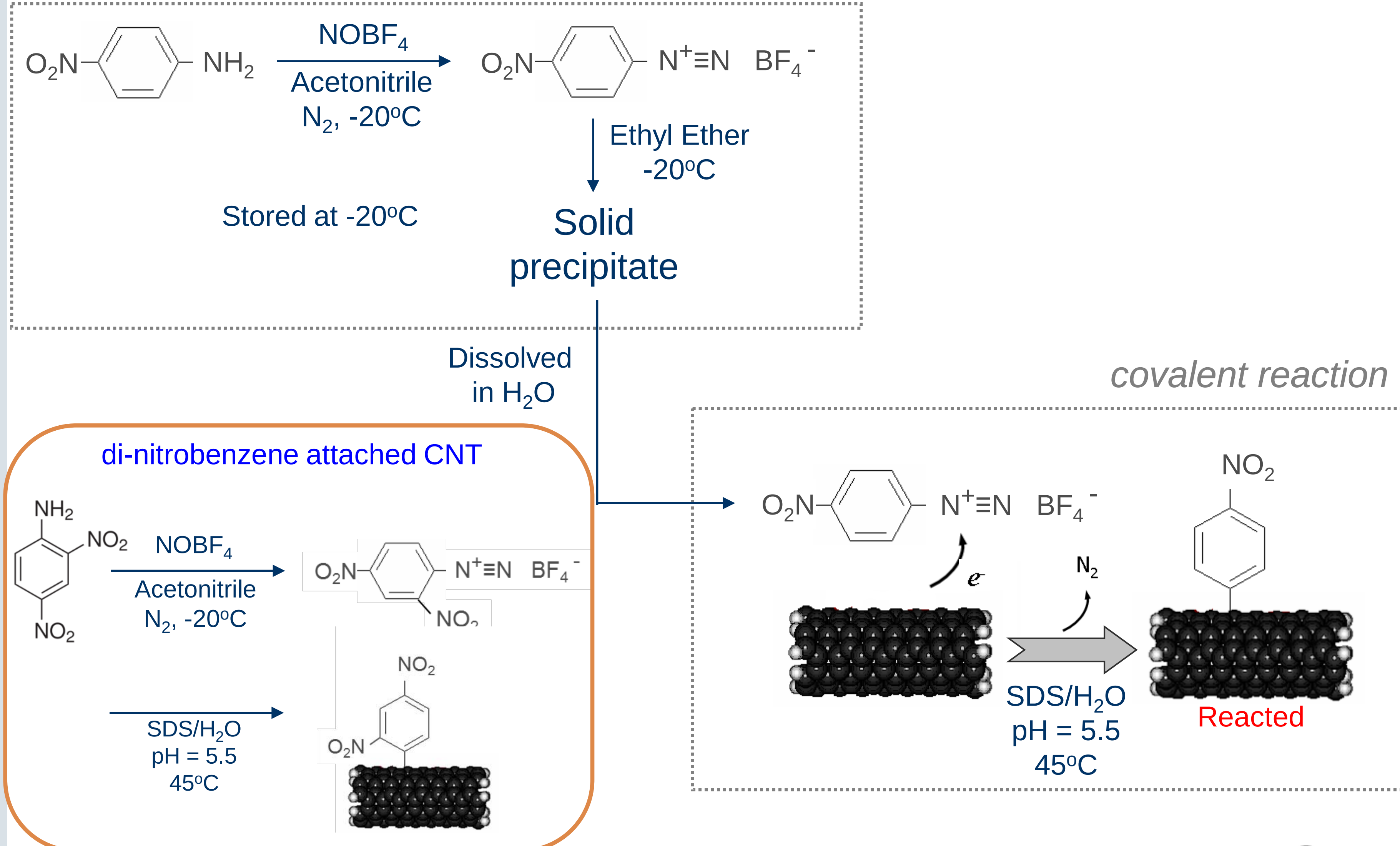
<u>Electron transfer reaction between CNT – Diazonium</u>

- 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

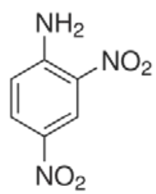
Covalent reaction scheme

mono- nitrobenzene diazonium synthesis

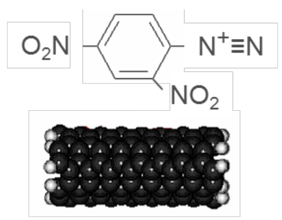


Experimental

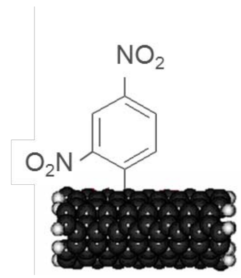
- **Energetic Materials Used**



di-nitroaniline alone

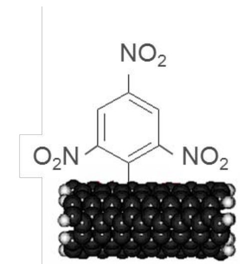


di-nitrobenezene Diazonium + CNT



di-nitrobenezene functionalized CNT

mono-nitrobenezene functionalized CNT



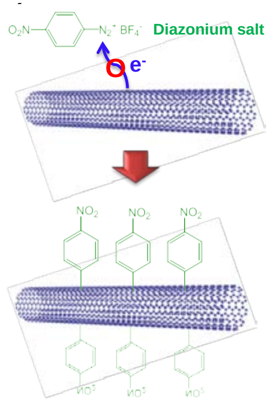
Physically mixed

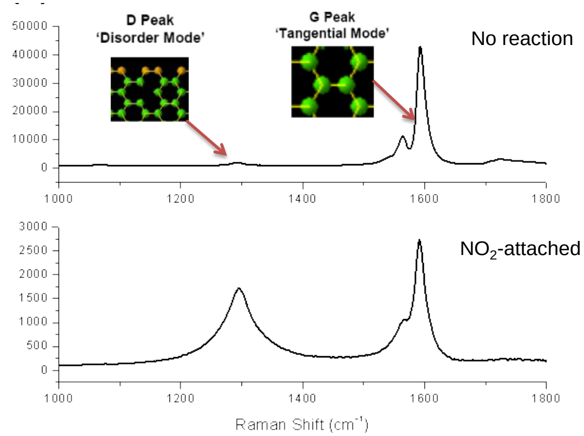
Chemically bonded

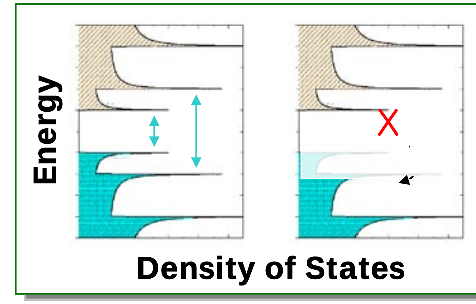
- **SWNT with different thermal conductivity used**

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

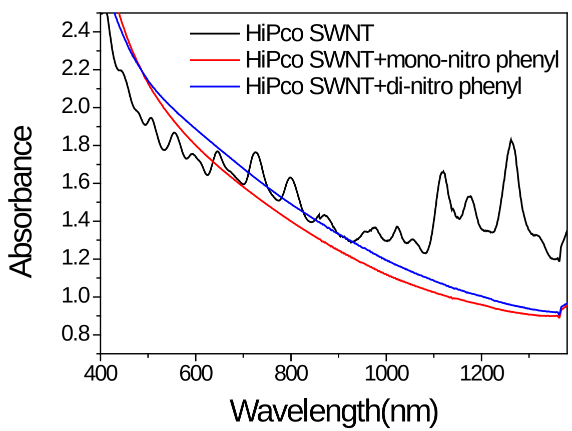
Energetic materials-CNT composites formation

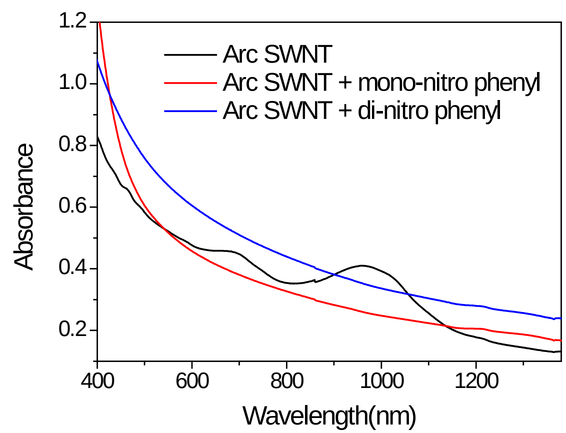


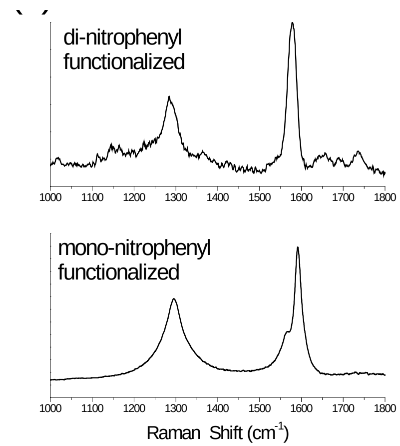




Reaction **Raman : D-band increases** **UV-vis-nIR: absorption decays**



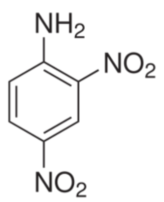
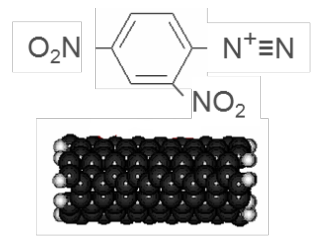
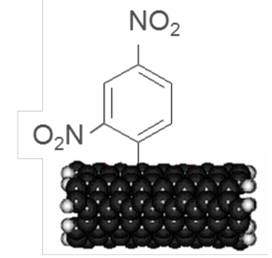
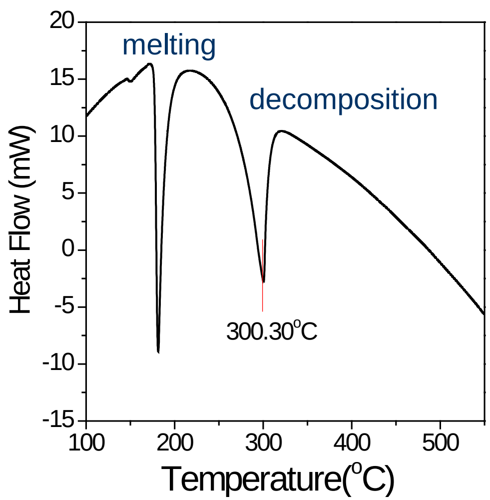
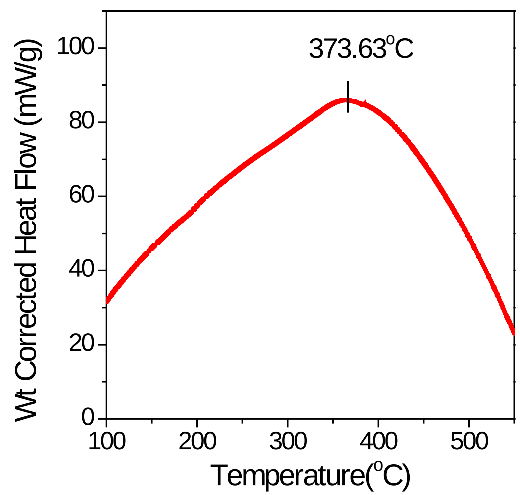
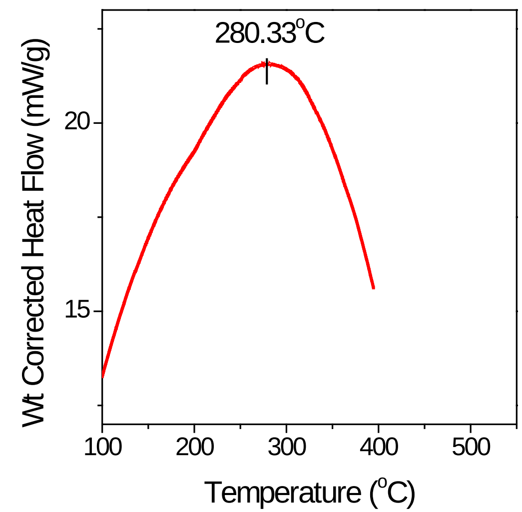




Nitrophenyl groups (energetic materials) successfully attached to SWNT (monolayer deposition)

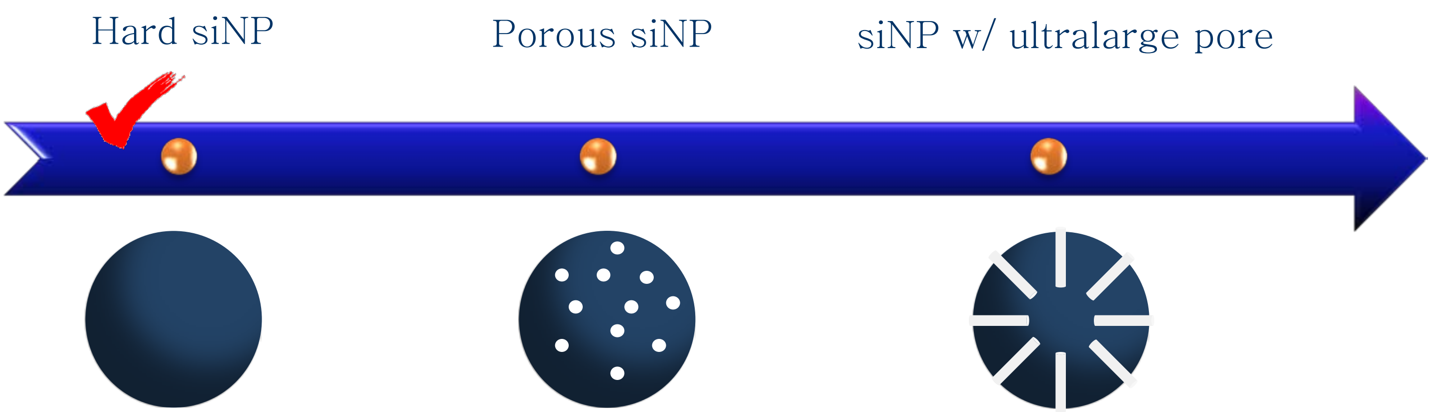
Energy Materials Converged

Chemical Attachment Effect

Alone	Physically mixed	Chemically attached
		
Di-nitroaniline	**Di-nitrobenezene + CNT mixture**	**Di-nitrobenezene functionalized CNT**
300.30 °C	**373.60 °C**	**280.33 °C**
		
Medium temperature	Broad range High temperature	Narrow range Lower temperature

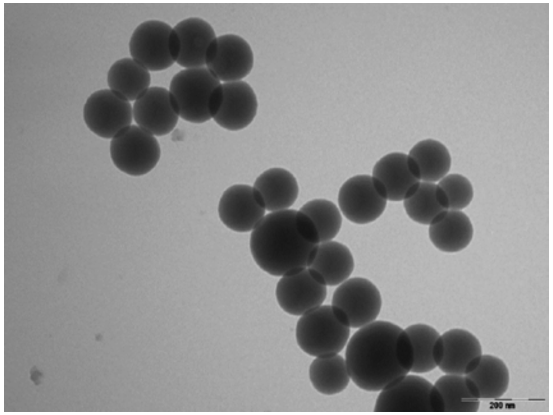
Experimental

- **Synthesis of silica nanoparticles as a template of nanoparticle.**

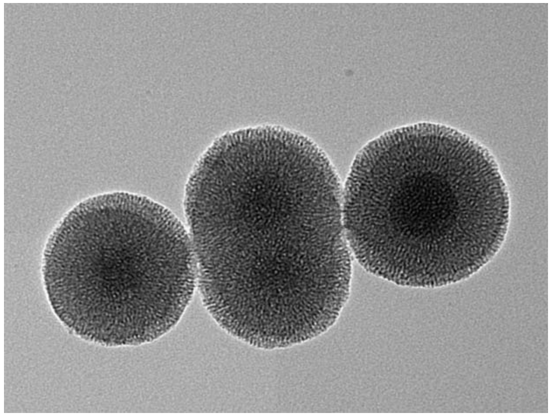


- **Synthesis of carbon nanoparticles**
  - $AlCl_3 6H_2O$ was added to strengthen the silica nanoparticles
  - Phenol and Paraformaldehyde was added and heated for 36h to generate carbon nanoparticles.

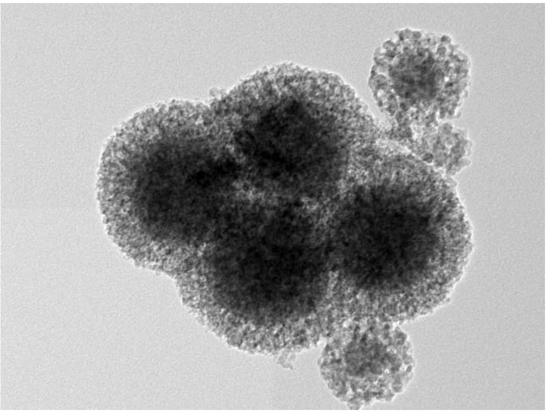
Synthesis of silica nanoparticles as a template of Porous Carbon Nanoparticle



sphere silica nanoparticles



Porous Layer coated Silica Nanoparticles



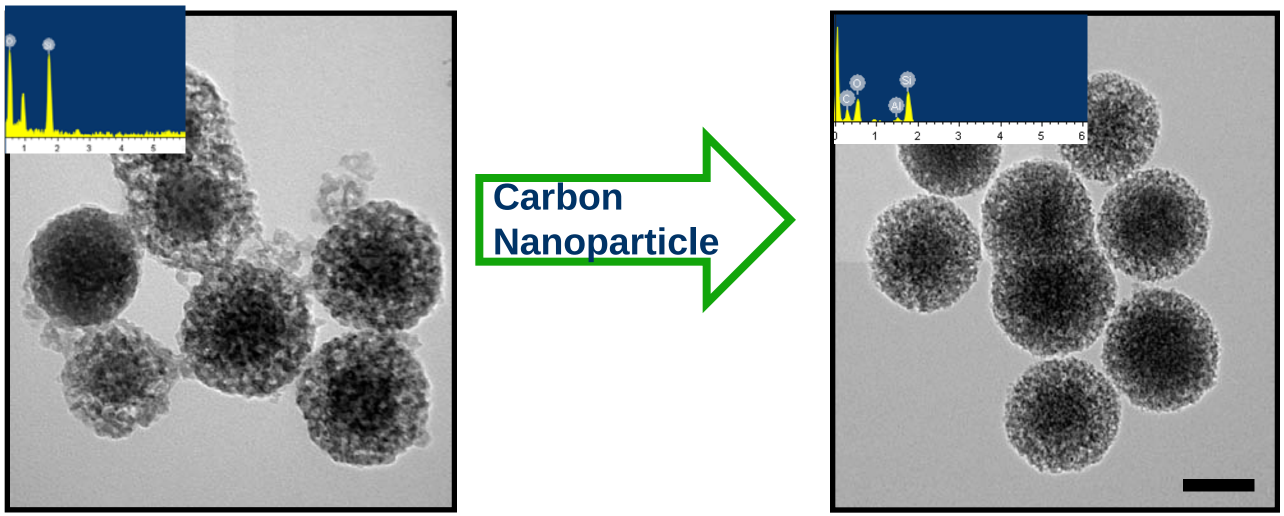
Pore-Enlarged Silica Nanoparticle

(scale bar : 50 nm)

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

Synthesis of Carbon Nanoparticle



(Scale Bar : 100 nm)

silica nanoparticles

Carbon materials coated nanoparticles

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 stabilizaing large amount of energetic materials.

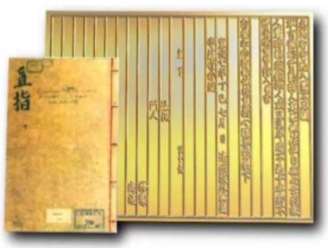
Energy Materials Converged

3rd KISHEM

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

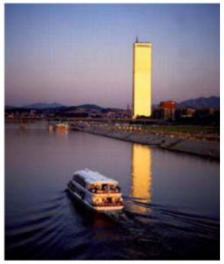

The world's oldest movable metal type invented by Korea and its printed evidence
Registered as Memory of the World, A.D. 1377


Gilt-bronze Seated Maitreya in Meditation
National Treasure No.78
Three Kingdom era (A.D. 200-700)

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**


Yonsei Univ.


Han River at night


Changdeokgung Palace (A.D. 1484) and Skyscrapers

Thank you for your attention!

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- Defense Acquisition Program Administration (DAPA)
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