과 학 기 술 부
21세기 프론티어연구개발사업
21st Century Frontier R&D Program

Driver to the future

APPLICATION OF NANOTECHNOGY ON HYDROGEN PRODUCTION AND STORAGE IN KOREA

April 26~27, 2007

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Director
Hydrogen Energy R&D Center
http://www.h2.re.kr

Outline

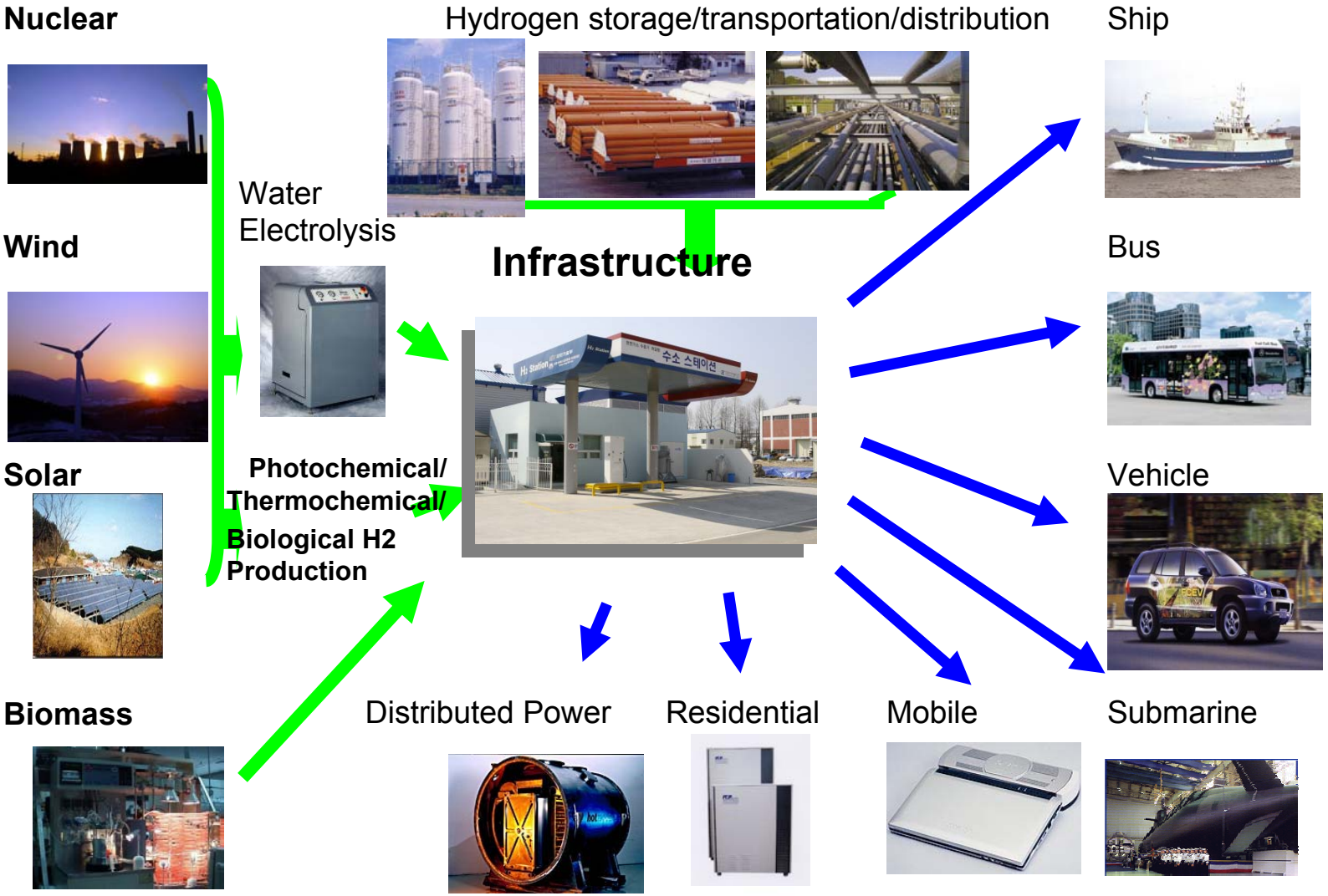
I. Hydrogen Economy- Vision

II. Technical barrier

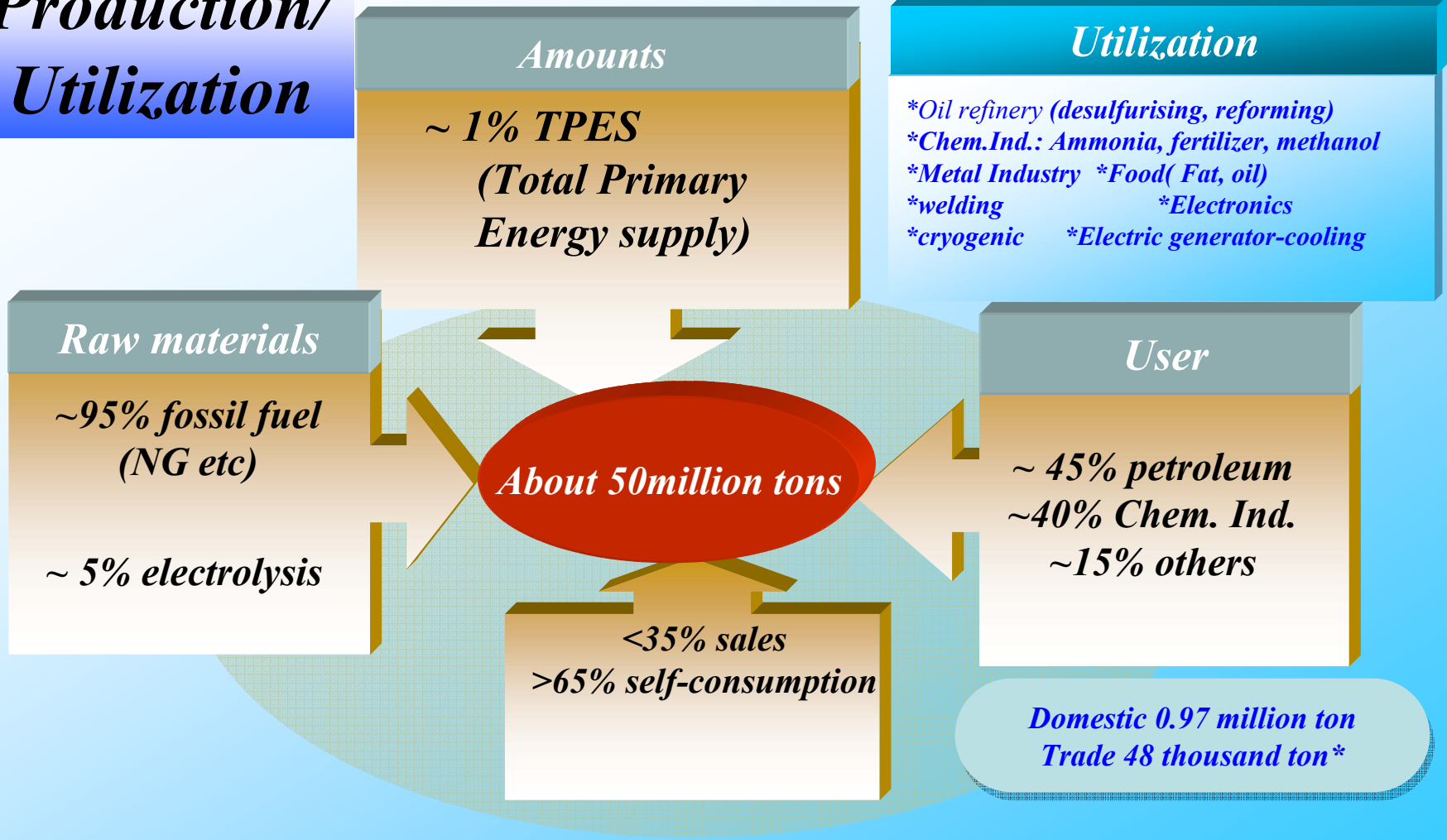
III. Current R&D activities related to nanotechnology

IV. Conclusions

Hydrogen Economy



Production/ Utilization



* Source: Bongjin Kim et al: "The status of domestic hydrogen production, consumption and distribution", Trans. Of the Korea Hydrogen and New Energy Society, 16(4)391-399(2005)

Summary of Hydrogen & Fuel Cell R&D program

Table 1. Hydrogen & Fuel Cell R&D program in Korea

Program	Sponsor	Period
21st Frontier Program (Hydrogen Energy R&D Center) (www.h2.re.kr)	MOST	2003-2013
National RD&D Organization for hydrogen and fuel cell (www.h2fc.or.kr)	MOCIE	2003-
Nuclear Hydrogen Development and Demonstration Project (NHDD) (www.hydrogen.re.kr)	MOST	2004-2021
Korea IGCC RDD&D Organization (www.igcc.or.kr)	MOCIE	2006-2014

MOCIE: Ministry of Commerce, Industry and Energy
MOST : Ministry of Science and Technology

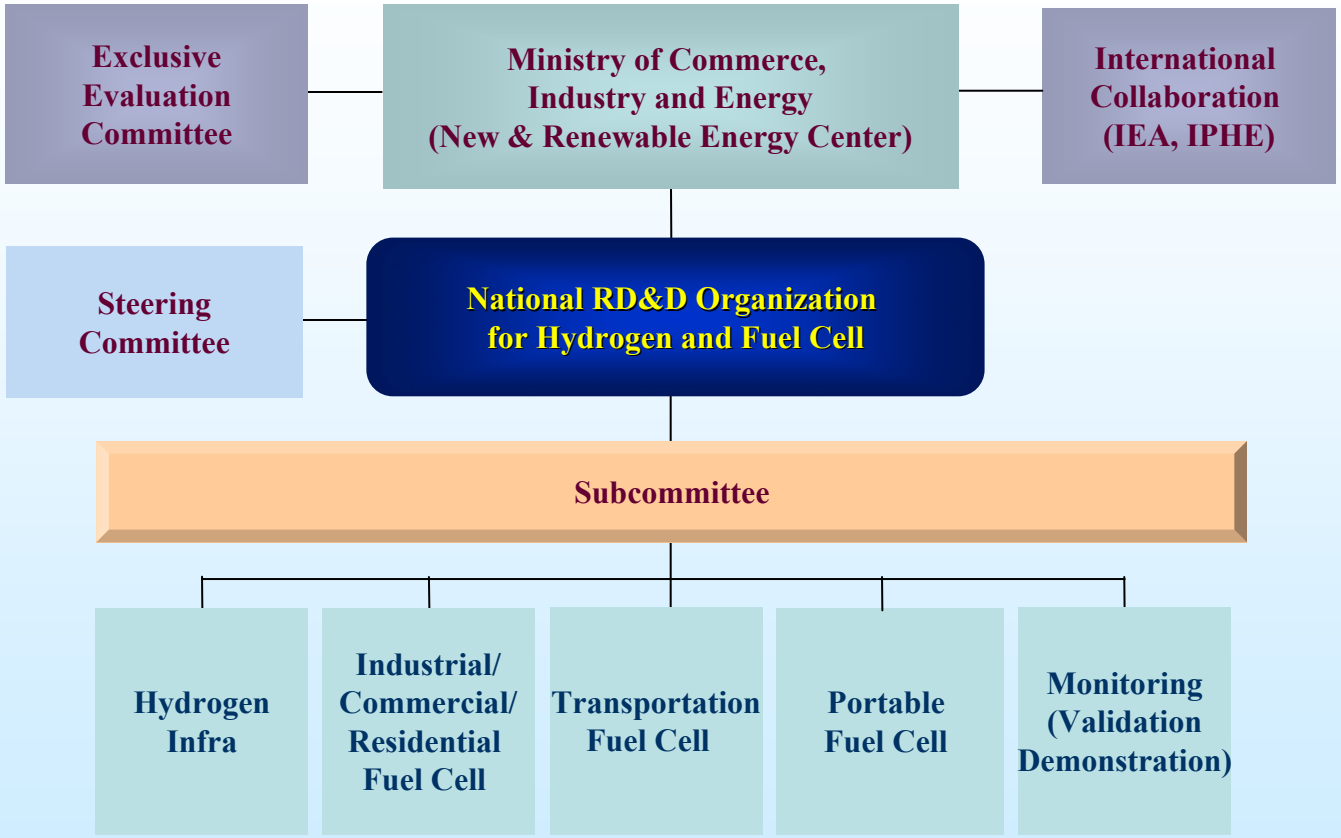
HERC

(Hydrogen Energy R&D Center)

- **Role**
  - Developing the National Hydrogen Energy R&D Program
  - * 21st Century Frontier Program
- **R&D Period**
  - 01 Oct. 2003 ~ 31 March 2013 (9.5 years for 3 phases)
- **R&D Fund**
  - Total 90 million US dollars
  - (Government : 80 million dollars, Industry : 10 million dollars)
- **Sponsoring Ministry**
  - Ministry of Science & Technology, Republic of Korea

Source: www.h2.re.kr

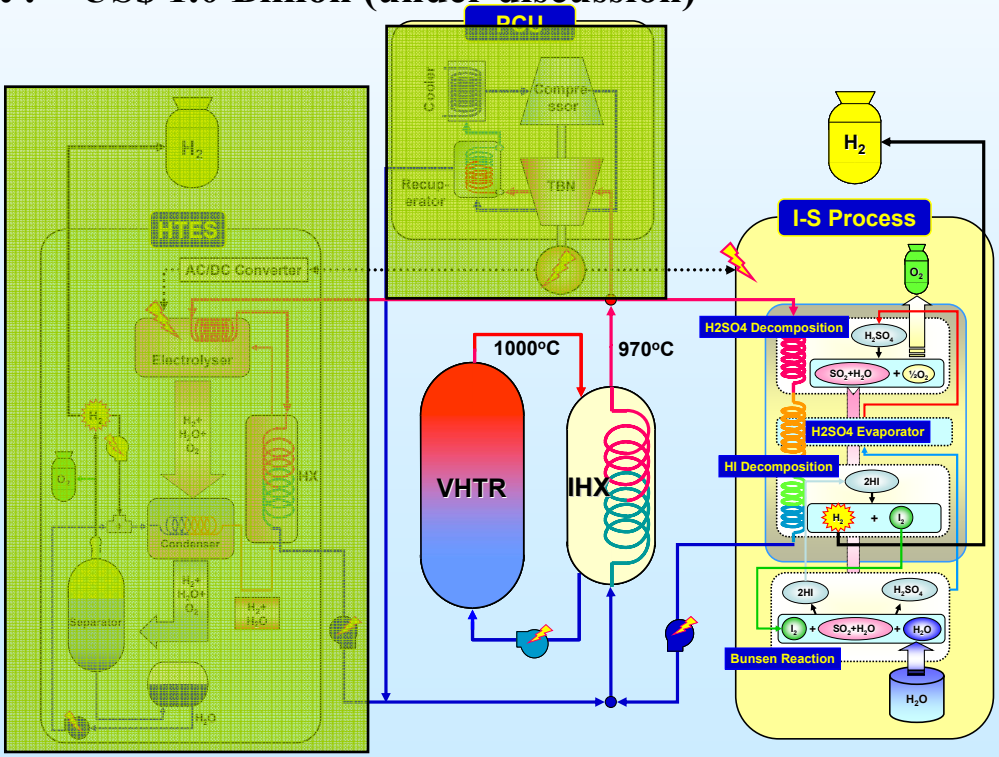
National RD&D Organization for Hydrogen and Fuel cell



- Established in 2003 to expedite the commercialization of hydrogen and fuel cell technology.
- Propose the vision for hydrogen economy in Korea.
- Develop a national plan, road maps and action plans to create a new industry.
- Coordinate and manage RD&D programs supported by government.

Nuclear Hydrogen Development and Demonstration Project

- **To build 200MWth class VHTR and to produce 20 thousand tons of hydrogen .**
  - **Period : 2004 – 2021 (18years)**
  - **Budget : ~ US$ 1.0 Billion (under discussion)**



Source: www.hydrogen.re.kr

☐ Korea IGCC RDD&D organization

MOCIE
(New and Renewable Energy Center)

Korea IGCC RDD&D Organization

*MOCIE; Ministry of Commerce, Industry and Energy

- **Launched on 22nd December, 2006**
- **In the year 2014, 300MW IGCC plant will be constructed and operated**
- **599.2 billion won (Government 165.2) .**

1st subdivision (Heavy industry, Research Institute)	**2nd subdivision (Power company, construction company)**	**3rd subdivision (Power company, Research Institute)**	**4th subdivision (Research Institute and University)**
Design of Gasification plant and process	Design, manufacture and construction of demonstration plant	Operation of demonstration plant	Localization of unit process

R&D Activities in the Phase II (HERC)(2006-2009)

	Action type	
Hydrogen Production		
▸ NG steam reforming for hydrogen station	(AR/DE)	(Mid)
▸ Biological hydrogen production	(BR/AR/DE)	(Long)
▸ Thermo-chemical hydrogen production	(BR/AR/DE)	(Long)
▸ Photocatalytic and photochemical hydrogen production	(BR/AR/DE)	(Long)
▸ Water electrolysis using PEM and THE	(BR/AR/DE)	(Long)
Hydrogen Storage		
▸ Hydrogen storage using metal hydrides	(BR/AR/DE)	(Long)
▸ Hydrogen storage using nano-structured materials	(BR/AR/DE)	(Long)
▸ Hydrogen storage using chemical hydrides	(BR/AR/DE)	(Long)
Hydrogen Utilization		
▸ Linear power/generation system of hydrogen combustion	(AR/DE)	(Long)
▸ Hydrogen sensor	(AR/DE)	(Long)
Supporting Project		
▸ Measurement techniques for hydrogen storage materials		
▸ Policy and technology assessment		

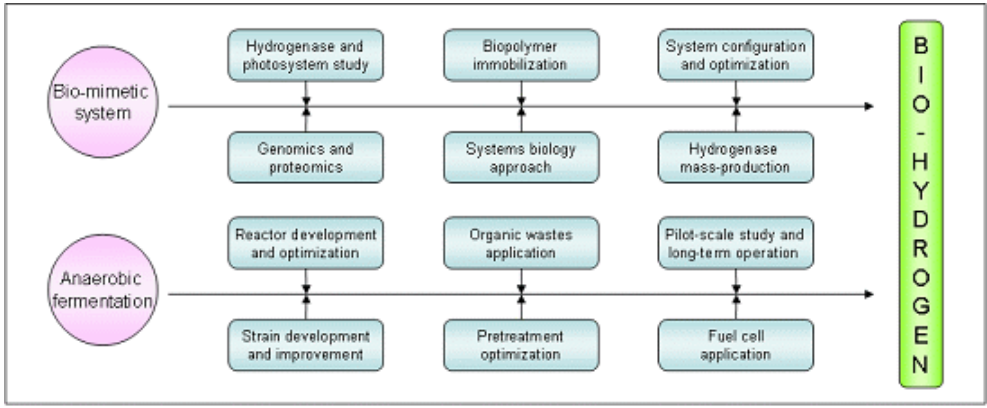
BR: basic research, AR: applied research, DE: demonstration

Biological Hydrogen Production

❖ R & D Objectives

-Scale-up and optimization of fermentative H_2 production process and development of bio-mimetic H_2 production system

- ▶ Fermentative bioreactor scale : > 500 L
- ▶ Fermentative H_2 productivity : 15 Nm^3 H_2/day/m^3
- ▶ H_2 productivity by bio-mimetic system : 40 L H_2/kg protein/hr



❖ Recent publications:
Int.J.Hydrogen Energy,31(2006)812-816
Int.J.Hydrogen Energy,31(2006)121-127
Korea Patent 2005-0032480

Bioreactors for photosynthetic and fermentative H_2 production

Project Manager: Dr. Kim, Mi-Sun,
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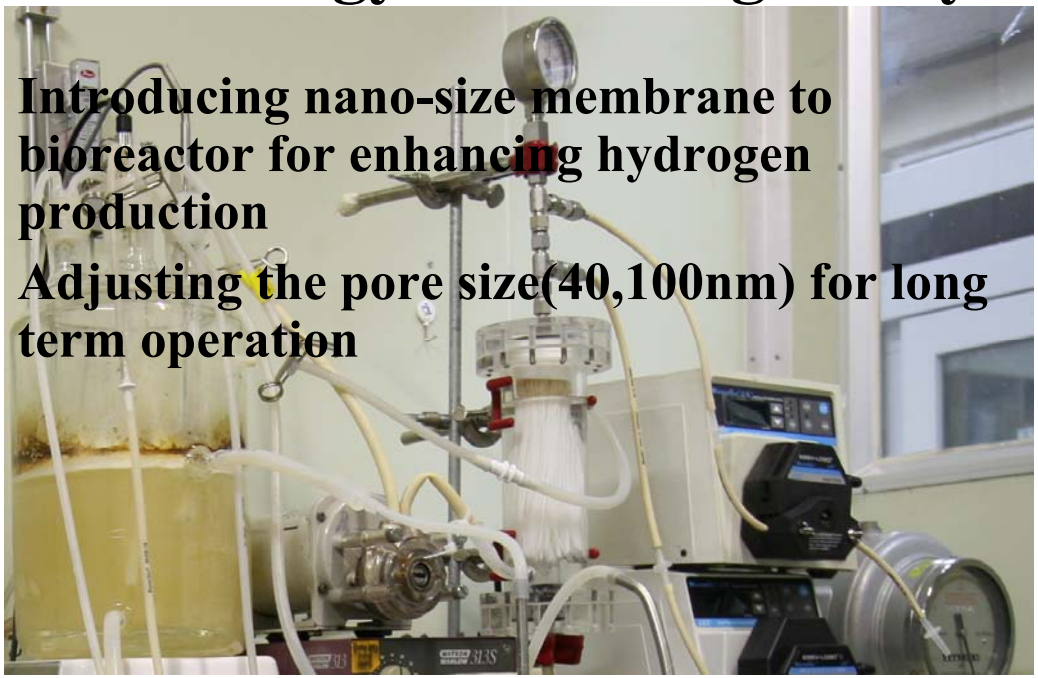
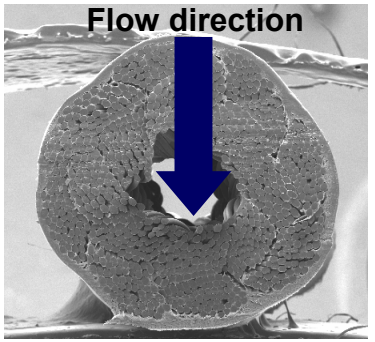
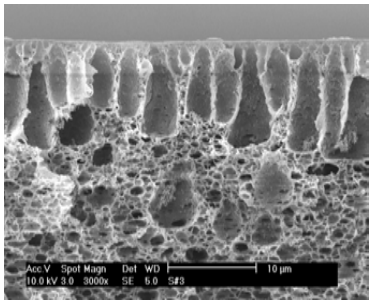
Nanotechnology and Biological hydrogen production

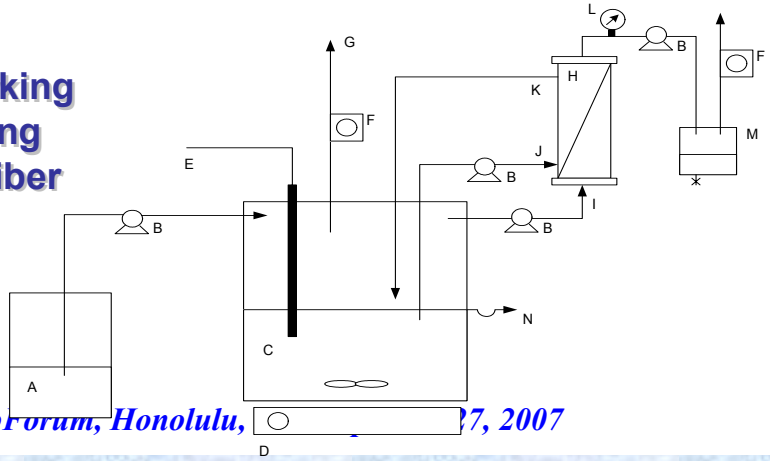
- Introducing nano-size membrane to bioreactor for enhancing hydrogen production
- Adjusting the pore size(40,100nm) for long term operation



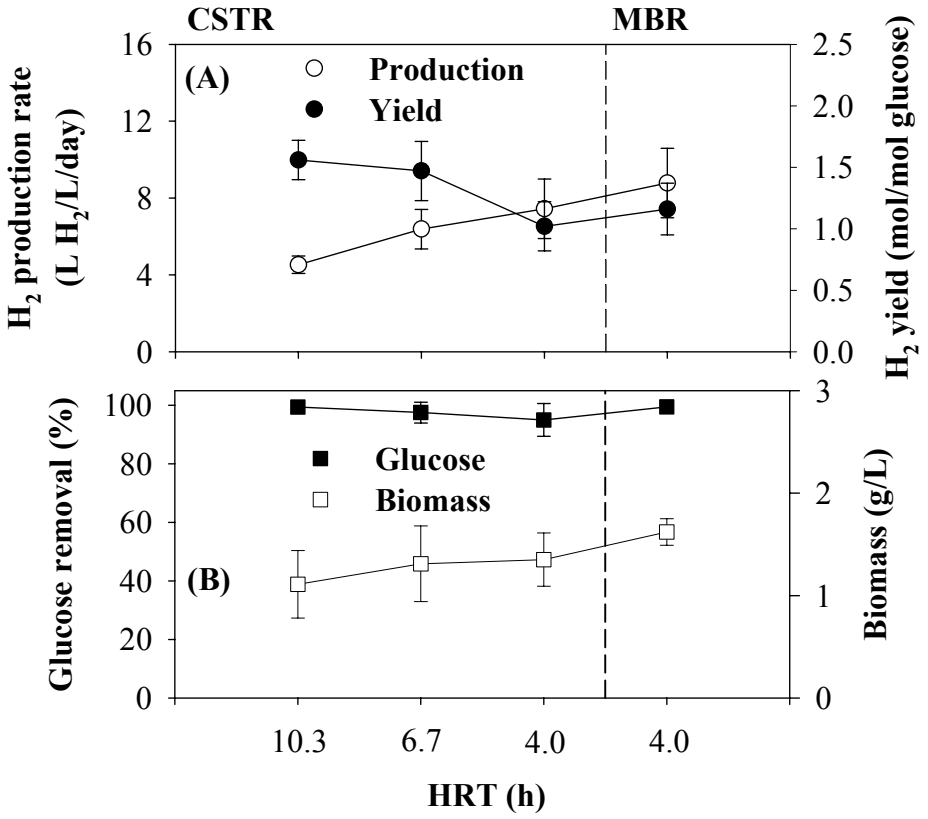


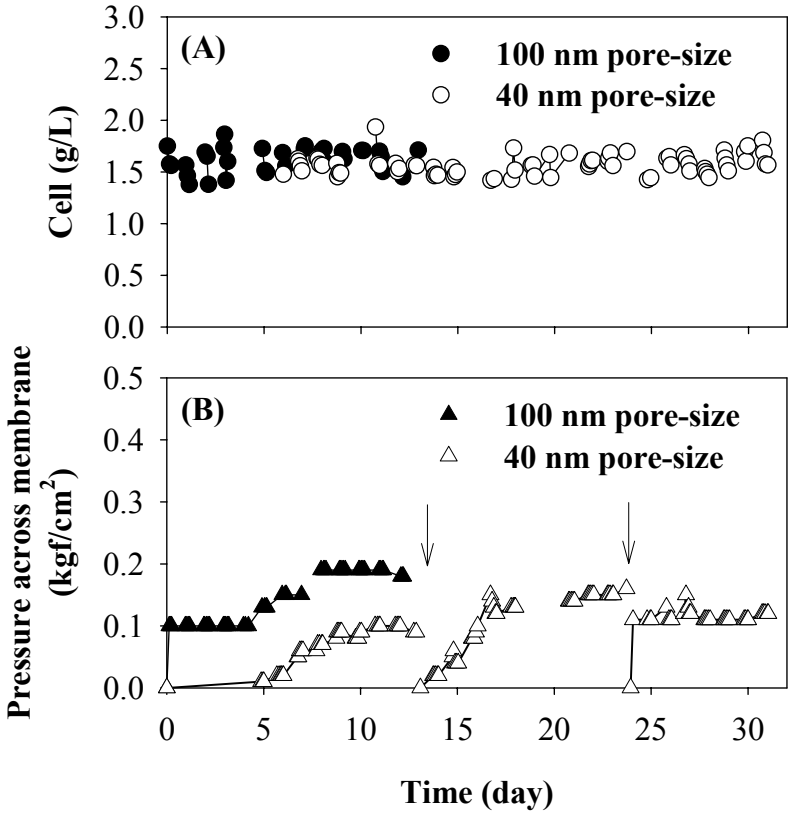


Membrane bioreactor (working vol. 2.4 L) using PVDF hollow-fiber

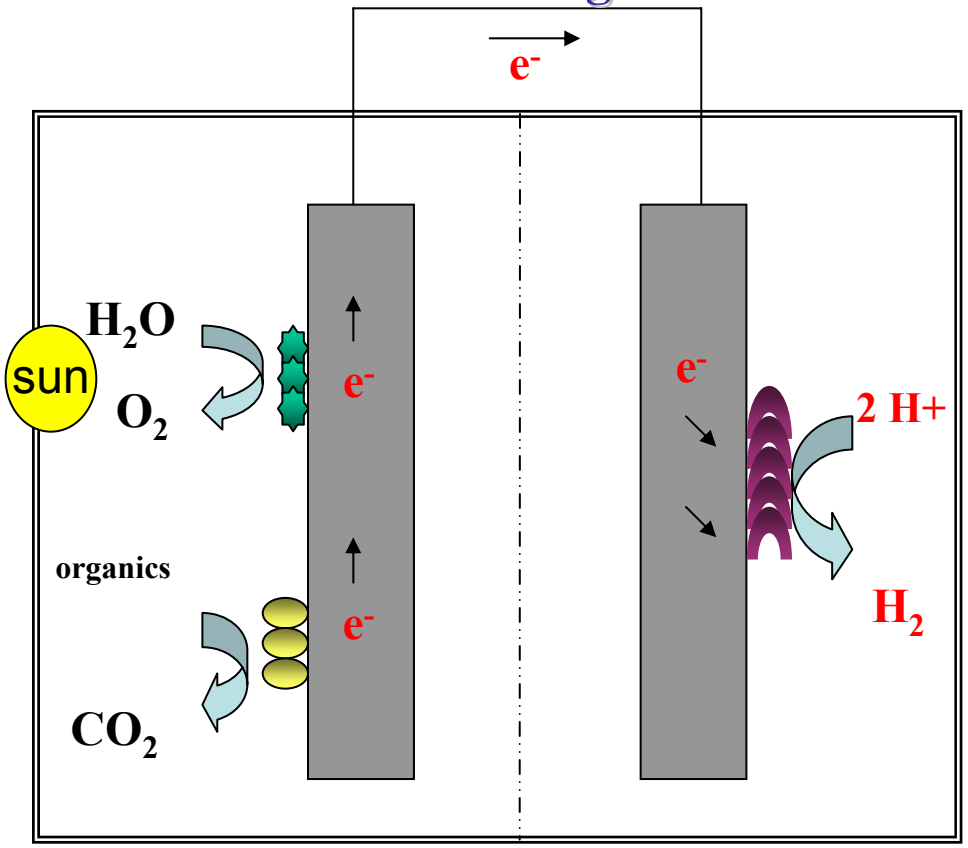


Hydrogen production using membrane bioreactor at 60°C





Schematic diagram of bio-mimetic H_2 production system



- photo-sensitizer (chlorophyil)
- microorganism
- hydrogenase

R&D Contents:

- **Electron donor/carrier (photosystem, microorganism)**
- **Biopolymer immobilization**
- **System integration**
- **hydrogenase**
  - o **separation/purification**
  - o **microorganism modification**
    - **Genome sequencing**
    - **Proteomes**

Photocatalytic and Photoelectrochemical Hydrogen Production Technology

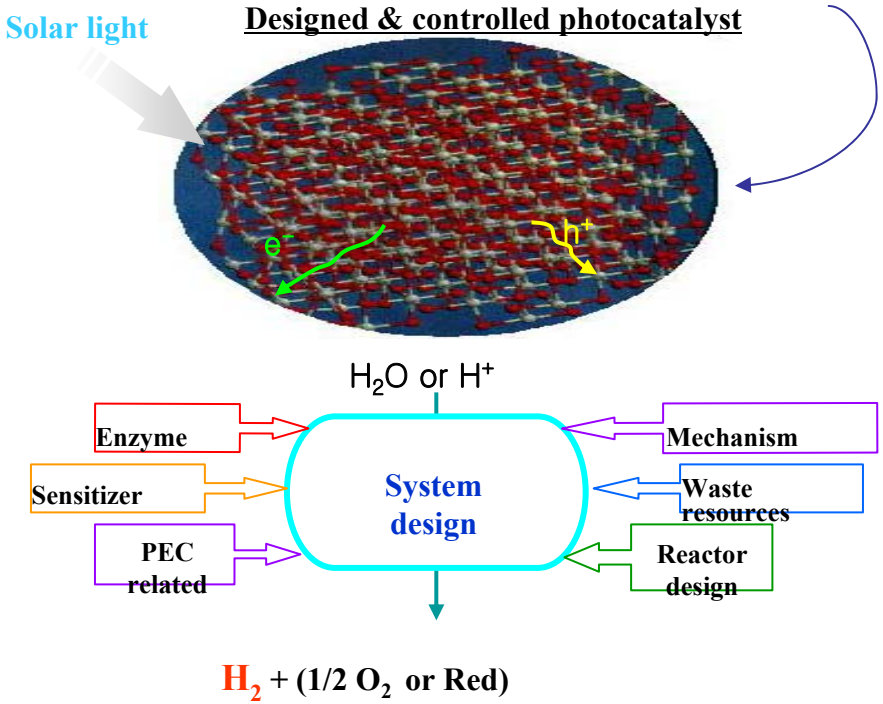
❖ R&D Objectives

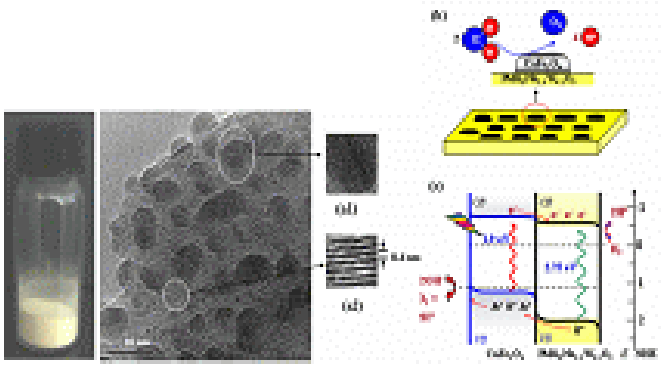
- Development of the system for 3% solar light conversion efficiency (@AM 1.5) utilizing solar light-sensitizing photocatalyst
- System establishment for PEC cell of 7% efficiency

❖ Content of R&D Activities

- Highly active water splitting photocatalysts- material design
- Tandem-type photoelectrochemical cell modules
- PEC cell of 7% efficiency
- Photo/Biocatalyst
- Q-sized photocatalysts and mesoporous media
- Layered Perovskite and Composite Photocatalysts

KRICT, KIER, KIST, POSTECH, Nanopac





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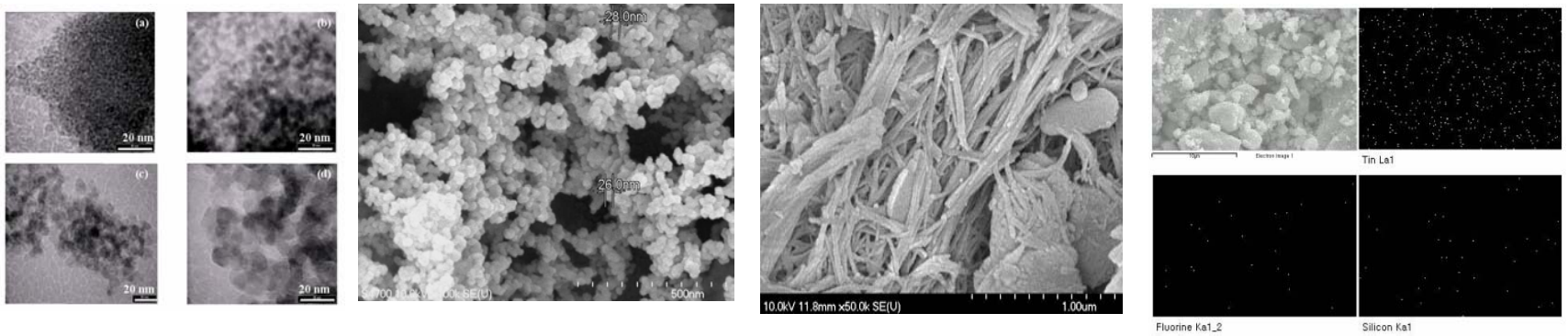
moonsj@krict.re.kr

Nanotechnology and sensor

- **Enhancement of gas sensitivity using ceramic nano particles with high surface area**
  - **Semiconductor type hydrogen sensor**

    - measure the change of resistance of semiconducting material (such as SnO_2, In_2O_3, TiO_2 etc) according to the adsorption of hydrogen gas. Nano sized semi-conducting material could enhance the sensitivity.
  - **Catalytic combustion type sensor**

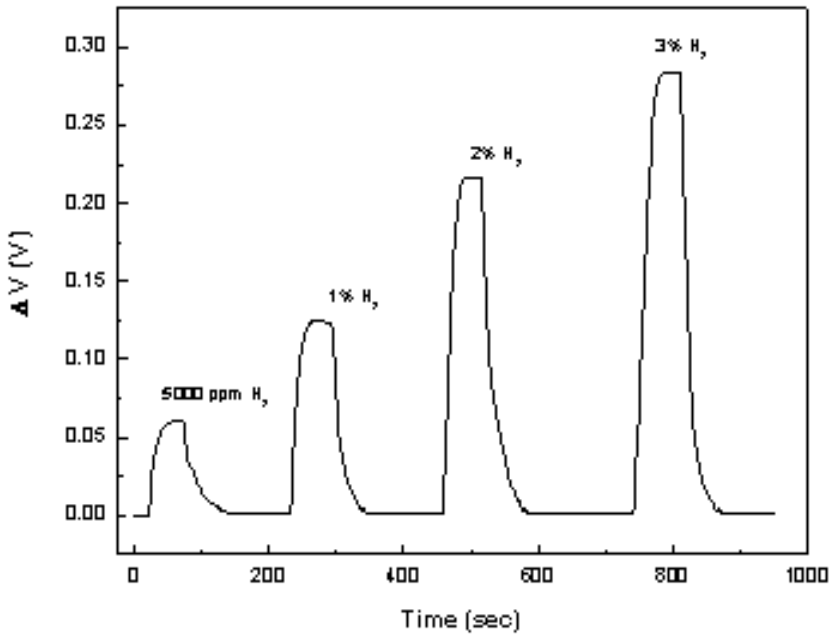
    - nano sized supporting material could enhance the sensitivity of sensor

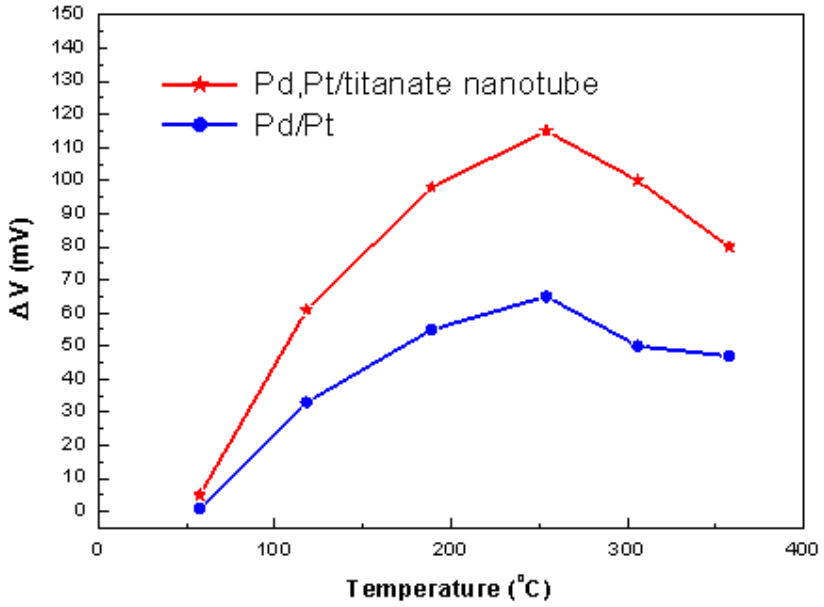


Chi-Hwan Han et. al, "Micro-bead of nano-crystalline F-doped SnO_2 as a sensitive hydrogen gas sensor", Sensors & Actuators B, 2005, 109, 264-269.

Chi-Hwan Han et. al, "Enhancement of H_2-sensing Properties of F-doped SnO_2 Sensor by Surface Modification with SiO_2", Sensors, 2006, 6, 492-502.

Enhancement of sensitivity using nano materials



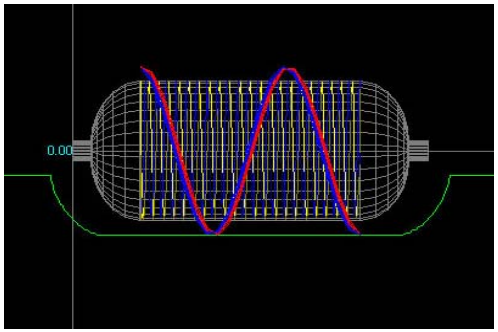


- Linearity of sensitivity of ceramic hydrogen sensor using nano particle

- Enhancement of sensitivity of catalytic combustion type hydrogen sensor using nano particle or nano rod of Pd/TiO_2, Pt/TiO_2

Pressurized hydrogen storage vessel

TYPE 3

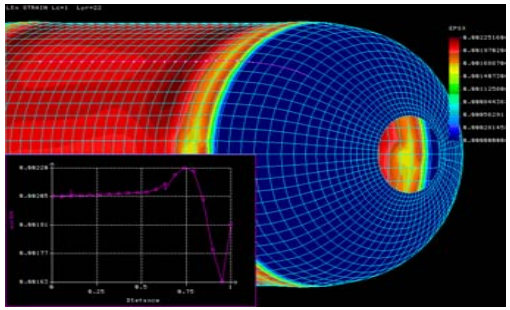


Process design and analysis

Filament winding and solidification

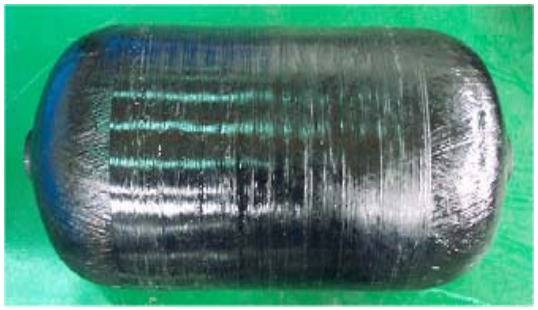
Proto type vessel

TYPE 4



Analysis using finite element method

liner



Storage vessel after coating process

Tucsan using a high pressure vessel

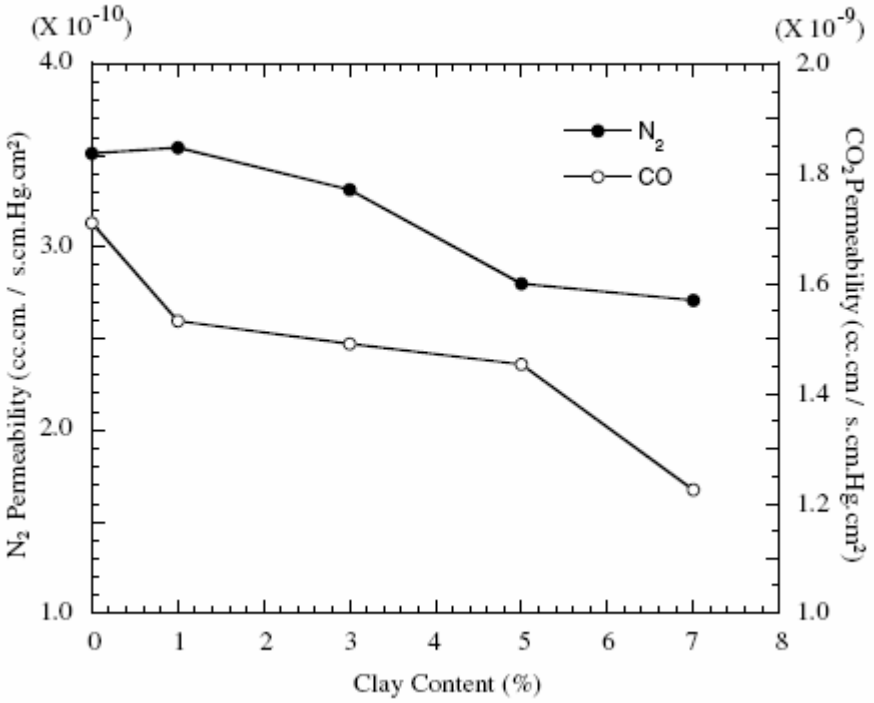


Fig. Gas Permeability of the nanocomposites for various clay contents

PE-Clay nano composite liner

: gas interrupting characteristic

-> increased to 30% than its predecessors

liner thickness

-> could be reduced.

7% clay-> the tensile modulus increased about 49%

the tensile strength increased about 15% as compared with pure polyethylene.

Source: Joong-Hee Lee et al, "Properties of polyethylene-layered silicate nanocomposites prepared by melt intercalation with a PP-g-MA compatibilizer", Composite Science and Technology (2005))

Effective hydrogen storage capacity < Target

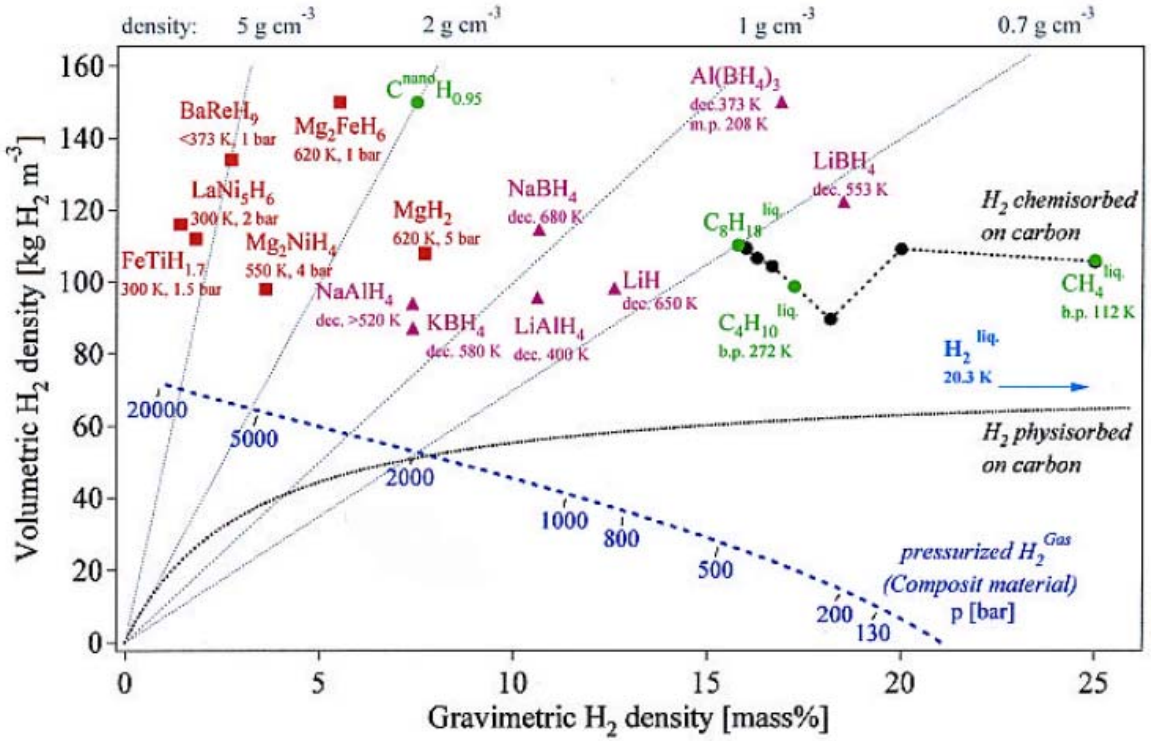
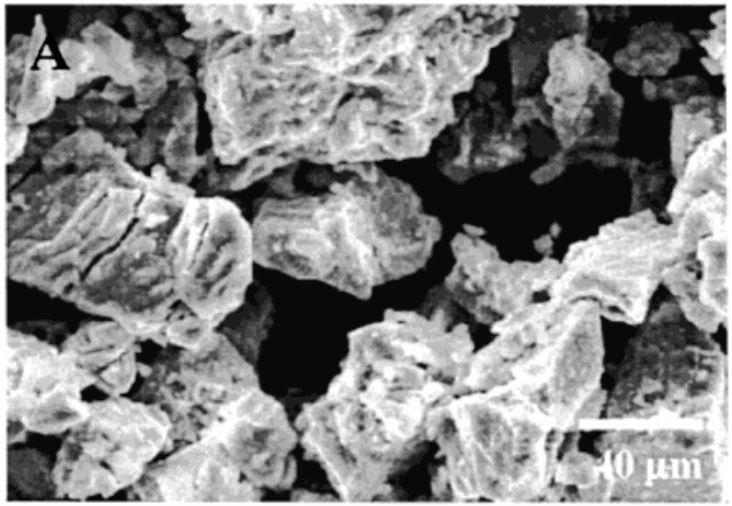
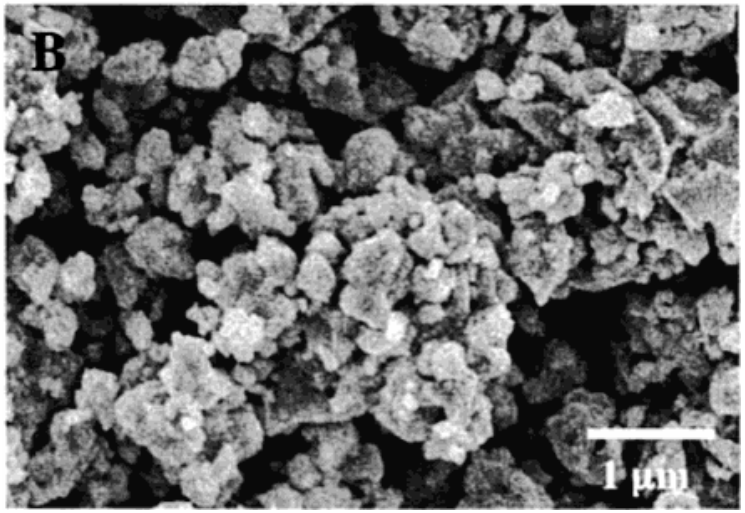


Figure 1 Storage density for various H_2 storage forms (Source: Schlapbach and Züttel, Nature, 2001 [1]).

Nanotechnology and Alanate

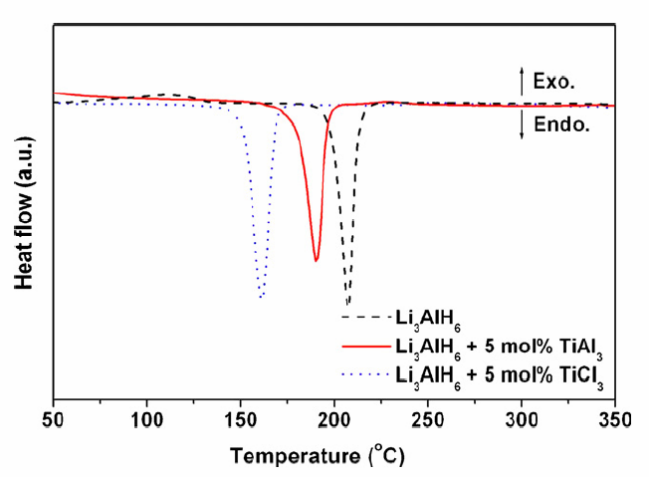
- Alanate- complex metal hydride with more than 5 wt% effective hydrogen storage capacity
- decomposition temperature of alanate
- Introducing nano sized particles
  - generating nanocrystallites through ball-milling
  - introducing the titanium nanoparticle as a catalyst

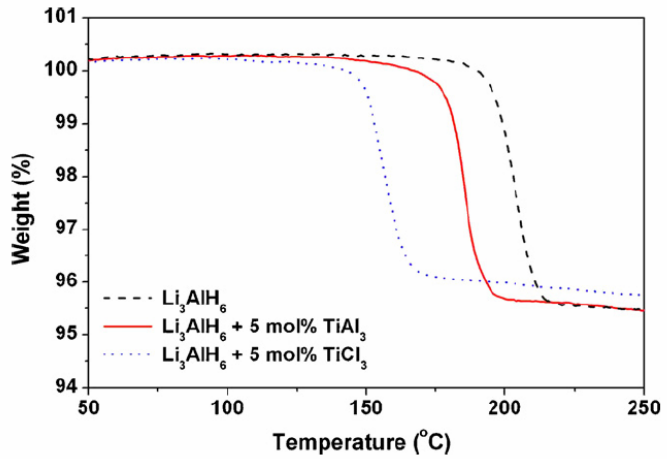




Ball-milling LiAlH4 and Li3AlH6 causes "the formation of a fine grain size below 20 nm ***(Chen et al.,2001)***

Lithium alanate system

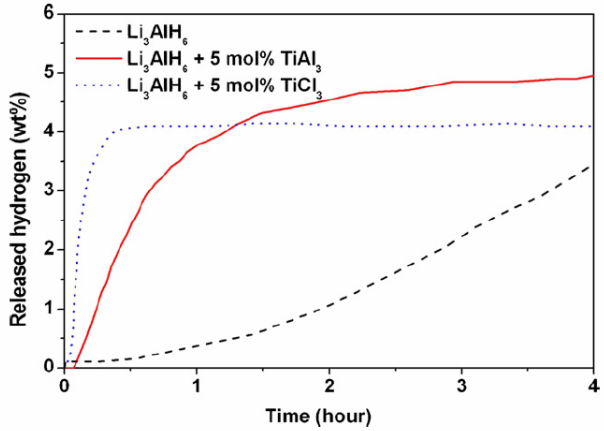




DSC and TG curves of Li_3AlH_6 with and without catalysts

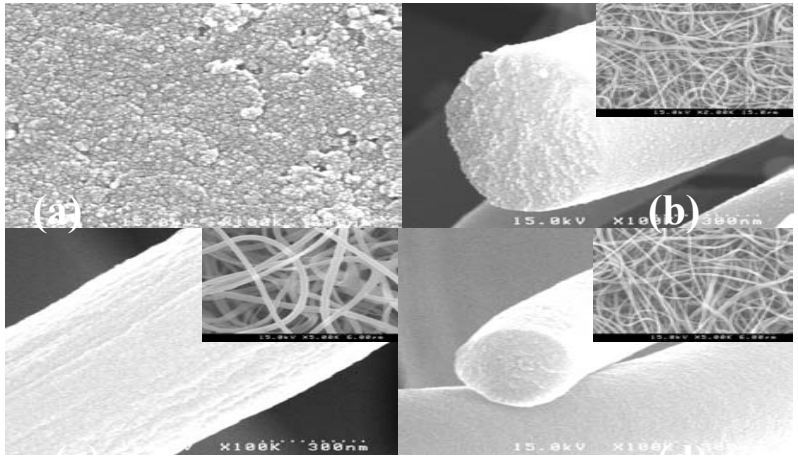
- Li_3AlH_6 -> 3 LiH + Al +3/2 H_2

Amount of hydrogen released from Li_3AlH_6 during thermal decomposition at 150°C as a function of time

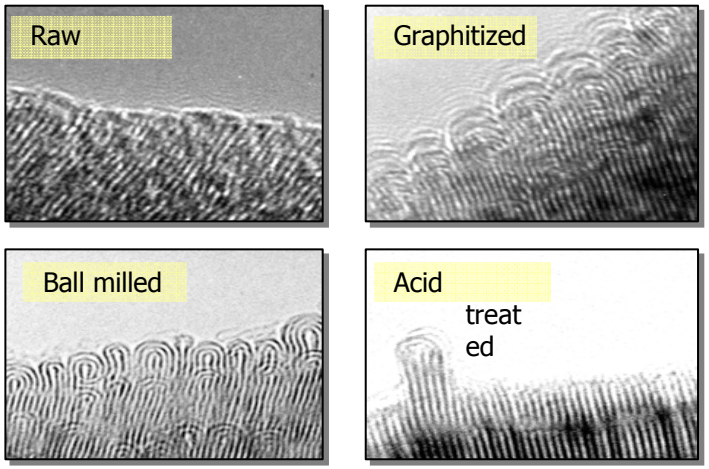


- Y.W.Cho et al, Thermal decomposition of Li3AlH6 with TiAl3 catalyst, catalysis today (Feb.2007)

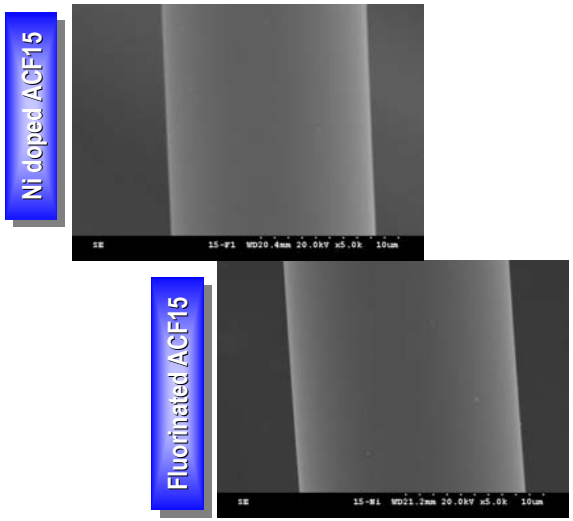
Carbon base nanomaterials

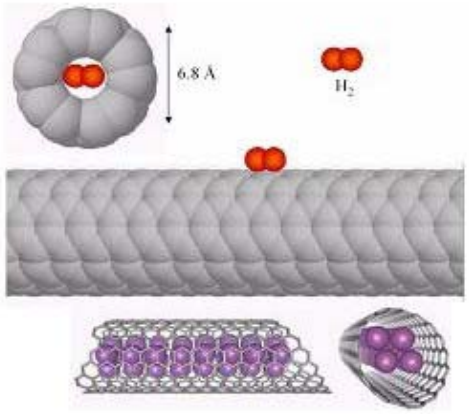


PVdF based Carbon Nanofiber

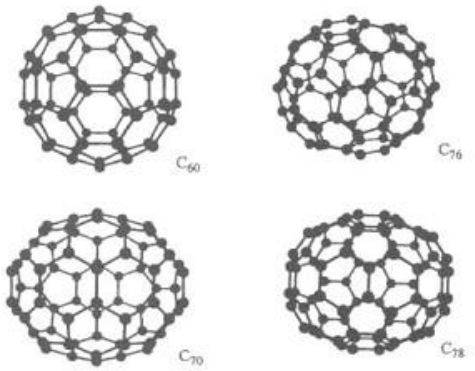


Surface Modified ACFs





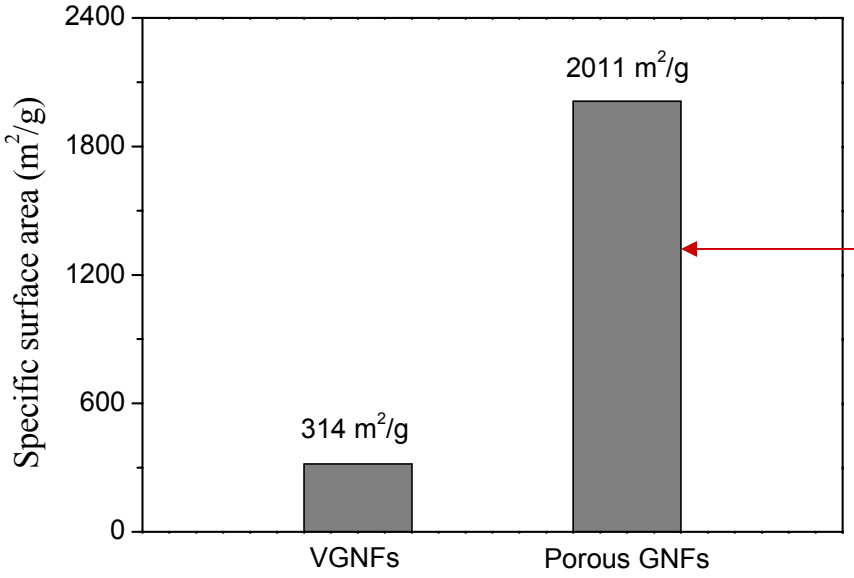
Hydrogen storage site of carbon nanotube

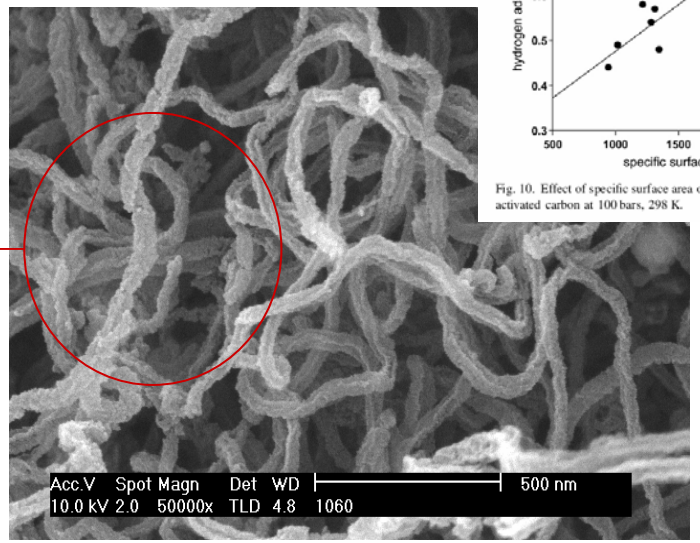


fullerene

Nanotechnology and carbon base materials

- **High surface materials with nano pore for high hydrogen storage capacity**
- **Nanopore exposition- surface oxidation at high temperature.**





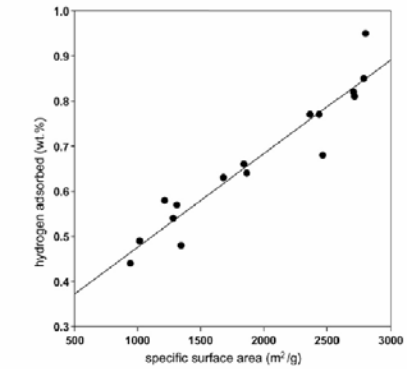


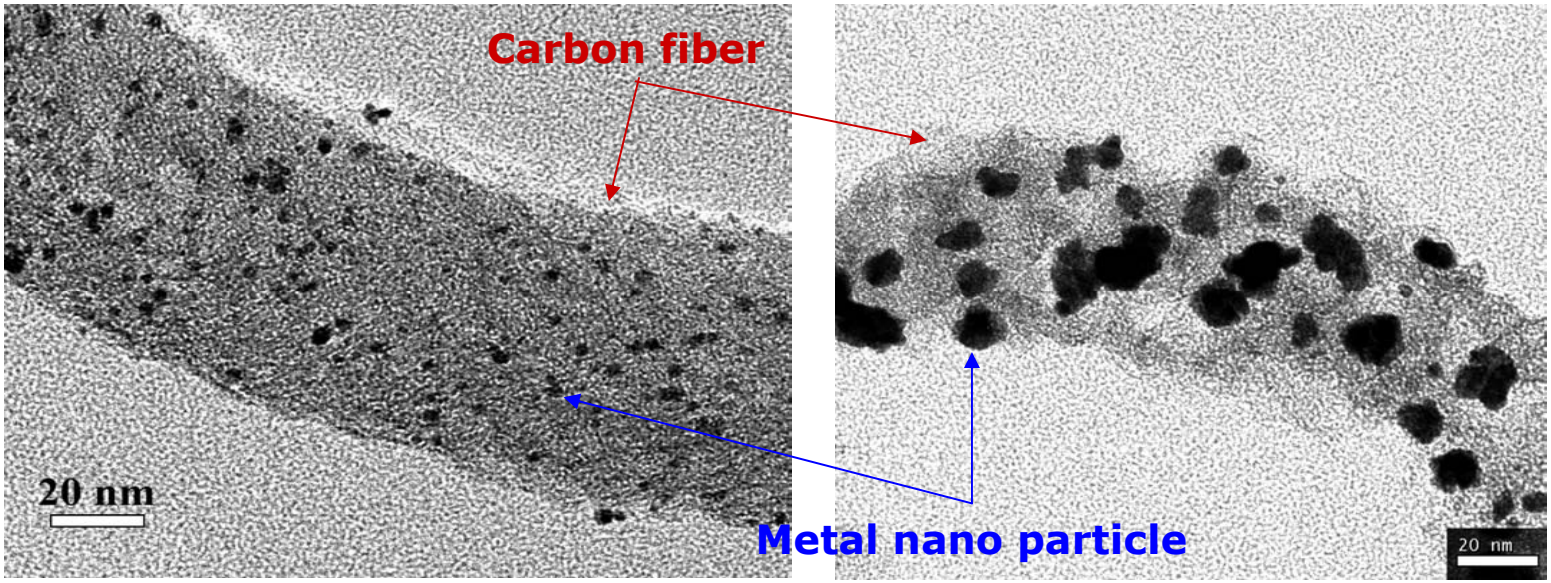
Fig. 10. Effect of specific surface area on the hydrogen adsorption capacity of activated carbon at 100 bars, 298 K.

Carbon nanofiber with surface area about 300 m^2/g could be changed to multipore nanofiber with high surface area (>2000 m^2/g) through a series of oxidation processes

Metal nanoparticle loading

- introduction of metal nano particles in order to control hydrogen adsorption sites

- introducing metal particles with controlled size- current density and time using electrolysis and non-electrolysis



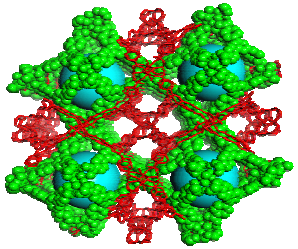
Introduction of Ni nanoparticle to the nanofiber surface using electrolysis and non-electrolysis

- Y.S,Lee et al, "The adsorption properties of surface modified activated carbon fibers for hydrogen storages", catalysis today (Feb.,2007)

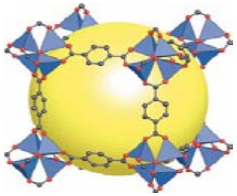
4. conclusions

- We have investigated various materials including MOF, organo-porous nanomaterial, inorganic materials based on molecular modeling and we attempted to improve surface functionality of those materials.
- But the hydrogen storage capacity is still low at moderate condition.

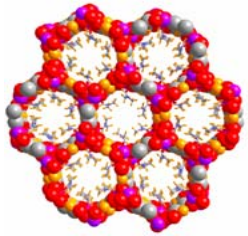
- We will investigate the mechanism for the adsorption of hydrogen on nanoporous material.
- we will setup the virtual screening protocol for the nanoporous materials.



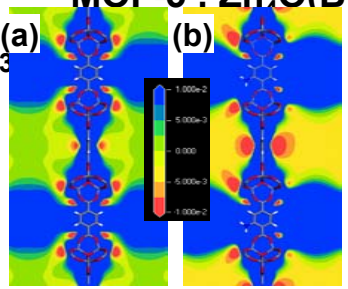
FeBTBC: $Fe_4O_2(BTB)_{8/3}$



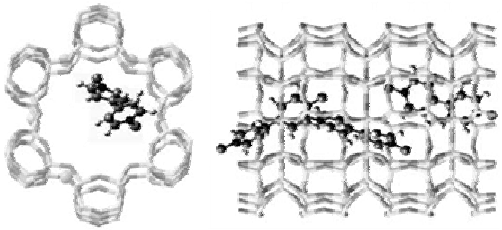
MOF-5 : $Zn_4O(BDC)_3$



Zn(dhBDC): $Zn_2O_2(BDC)$



Contour Maps of electrostatic potentials ; (a) IRMOF-1, (b) IRMOF-3



Think Together!

- There are lots of hurdles to hydrogen production and storage
- Nanotechnology will help to overcome those barriers.

❖ There is nothing either good or bad. But thinking make it so.

❖ Value is always every where!