Nanoparticle Technology

Lecture 10: Nanomaterials Application

중앙대학교
CHUNG-ANG UNIVERSITY

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Introduction to Nanomaterials Application

In our previous lectures…

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Lecture 08~09: Nanomaterials Characterization	Optical spectroscopy: UV-vis, FT-IR, Raman Electron spectroscopy: XPS, EDS

Based on our previous lectures…

nature materials

ARTICLES

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Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts

Deli Wang[1†], Huolin L. Xin[2†‡], Robert Hovden[3], Hongsen Wang[1], Yingchao Yu[1], David A. Muller[3,4], Francis J. DiSalvo[1] and Héctor D. Abruña[1★]

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Citation number: 1384 (2020/11/27)

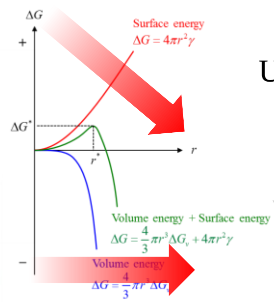
Based on our previous lectures…

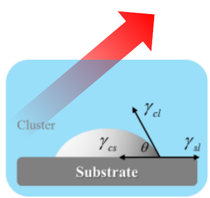
Methods for sample preparation

H_2PtCl_6 powder

$CoCl_2$ powder

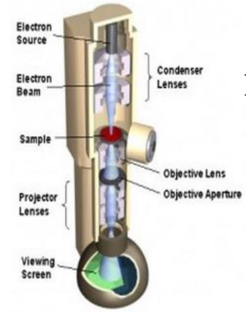
C powder



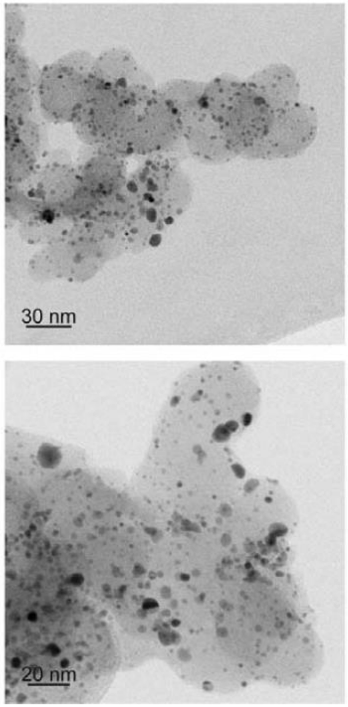


Ultrasonication
(30 min)

H_2/N_2 (150 °C, 2 h)
H_2 (400 or 700 °C, 2 h)

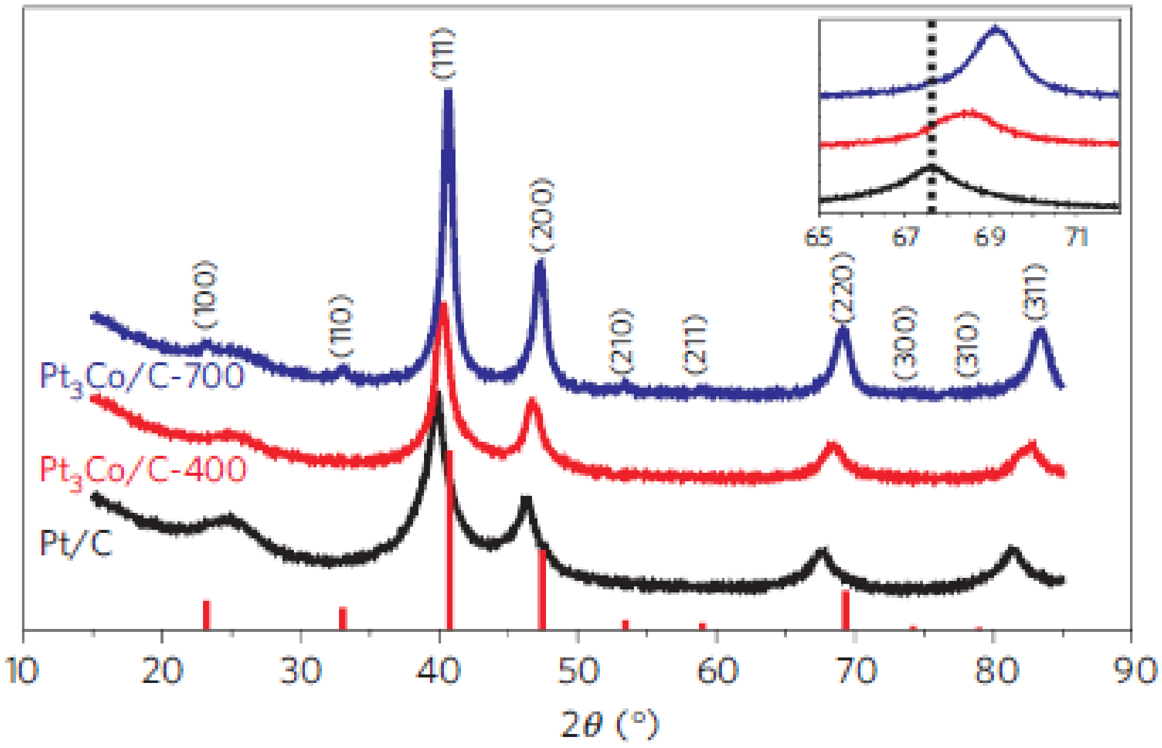


Pt_3Co/C-700 nanoparticles

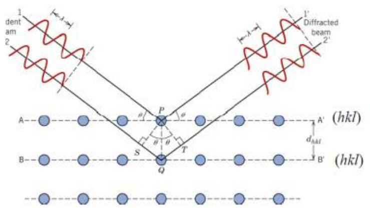


Based on our previous lectures…

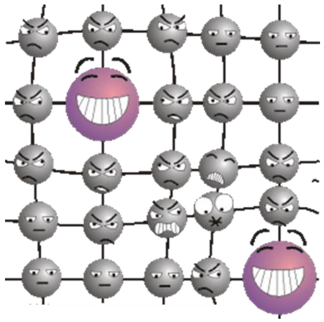
Crystal structures: XRD



Bragg's Law: $n\lambda = 2d_{hkl}\sin\theta$



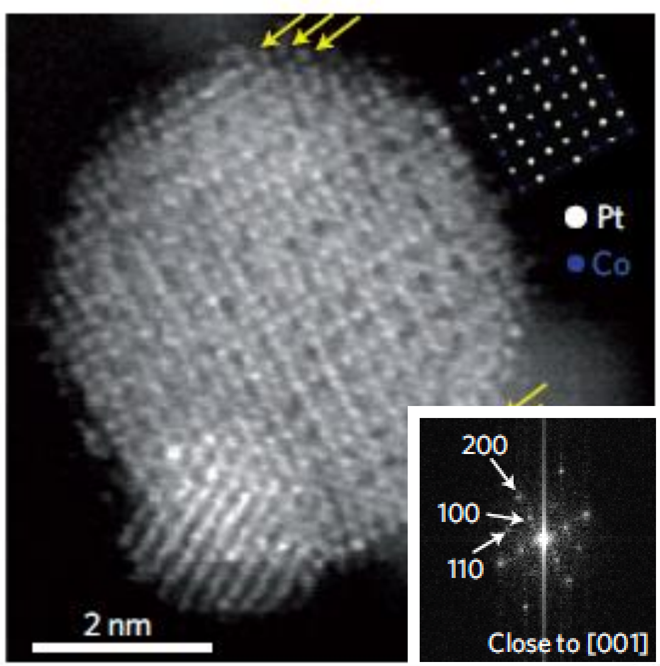
Crystal structure of alloy

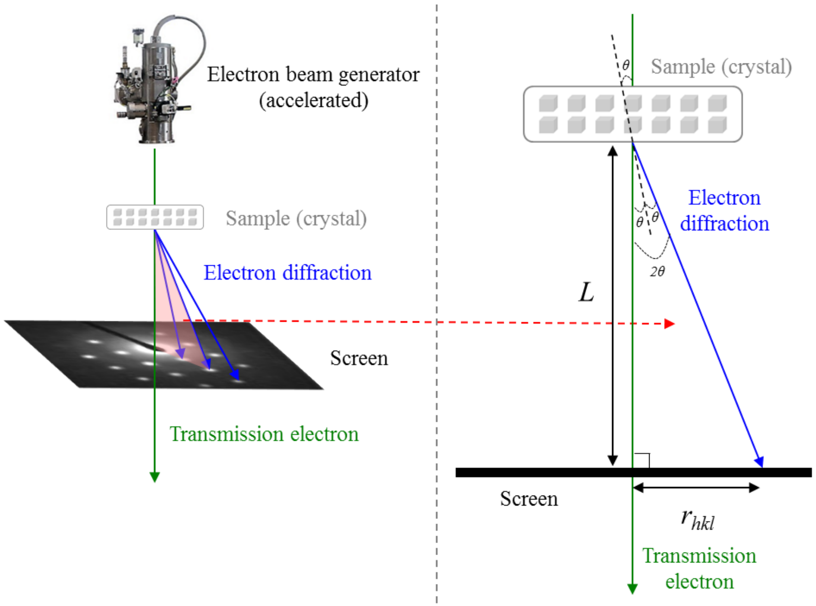


Atomic radius
Pt: 177 pm
Co: 152 pm

Based on our previous lectures…

Crystal structures: electron diffraction

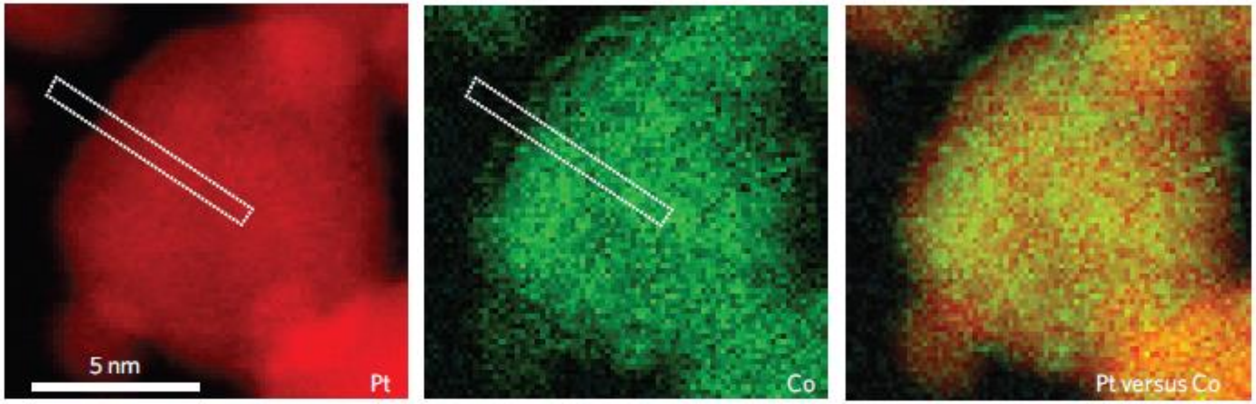


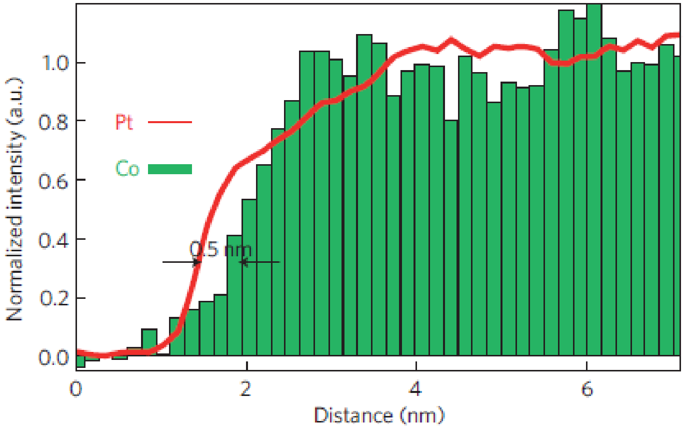


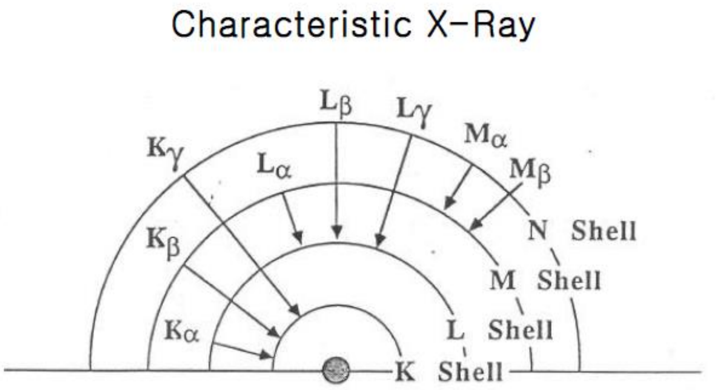
$$\lambda L = r_{hkl} d_{hkl}$$

Based on our previous lectures…

Elemental composition: EDS mapping and line scanning

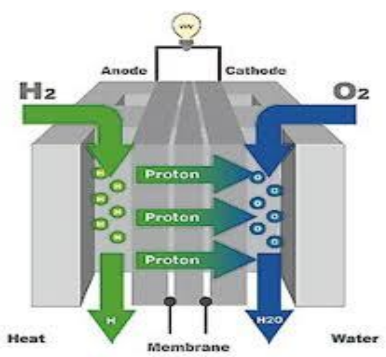






Based on our previous lectures…

Catalytic activity and stability of oxygen reduction reaction?

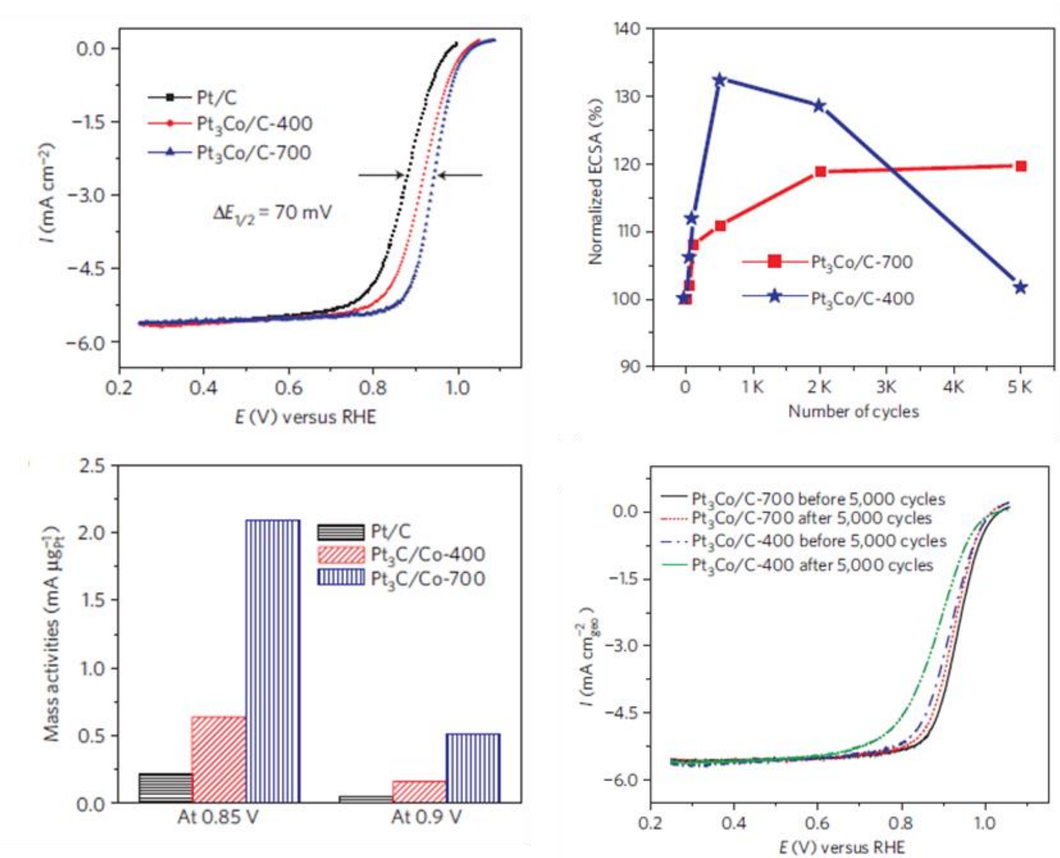


At anode: hydrogen oxidation reaction

$2H_2 \rightarrow 4H^+ + 4e^-$

At cathode: oxygen reduction reaction

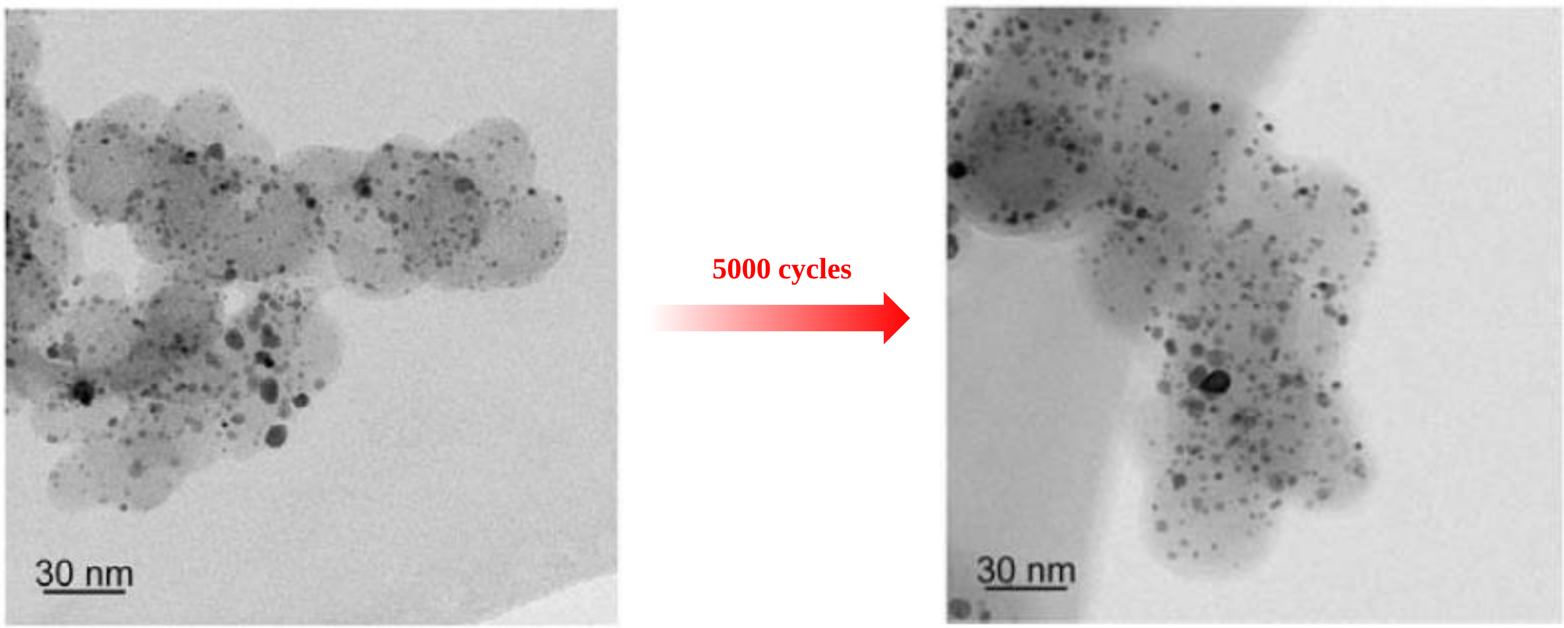
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$



Nanoparticle Technology

Based on our previous lectures…

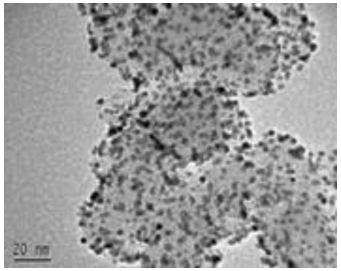
Stability of nanoparticles (Oswald ripening?)



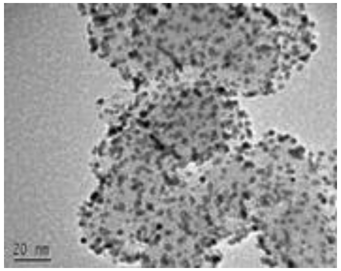
Nanotechnologies in Fuel Cell

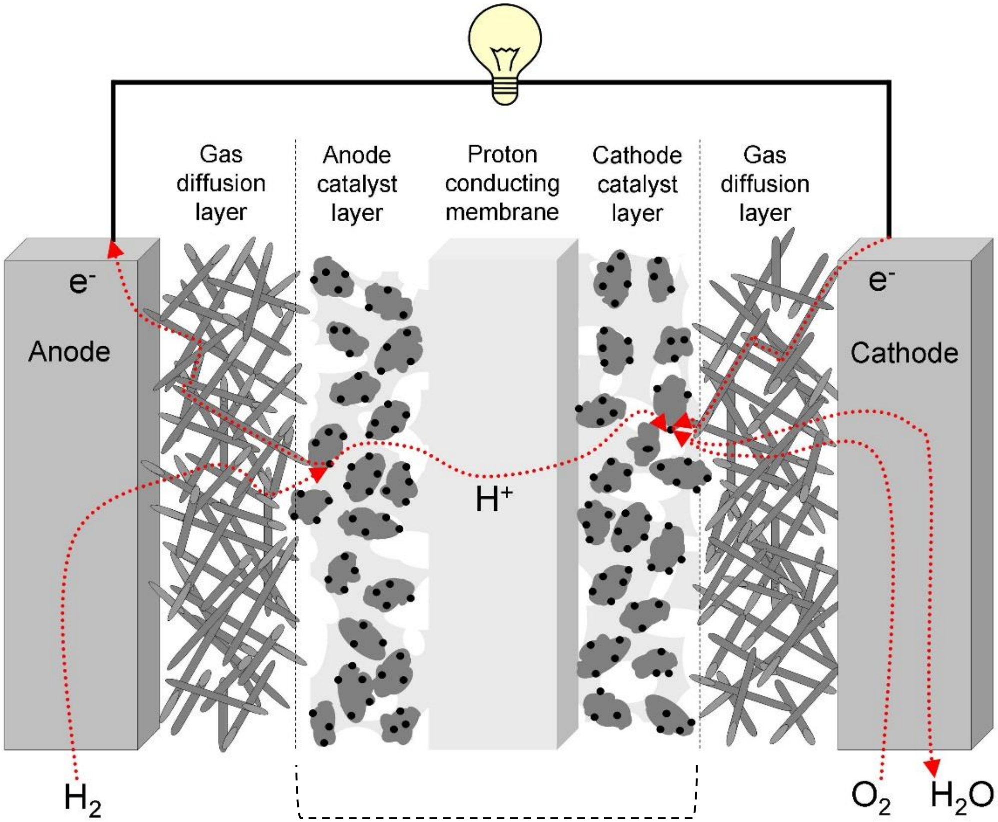
Pt/C nanoparticle catalysts for fuel cells

Pt/C



Pt/C





Membrane electrode assembly (MEA)

Anode reaction:

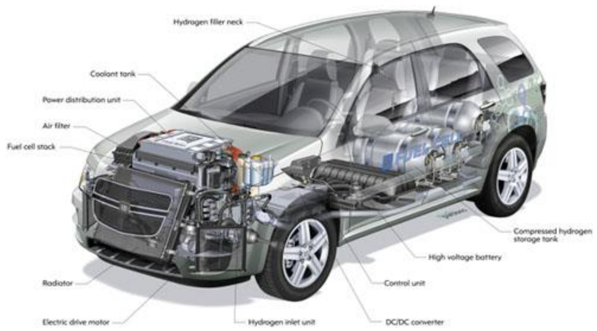
$2H_2 \rightarrow 4H^+ + 4e^-$

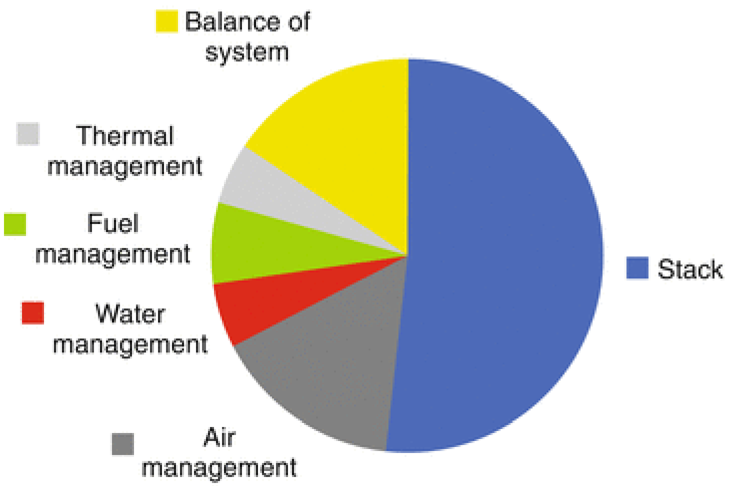
Cathode reaction:

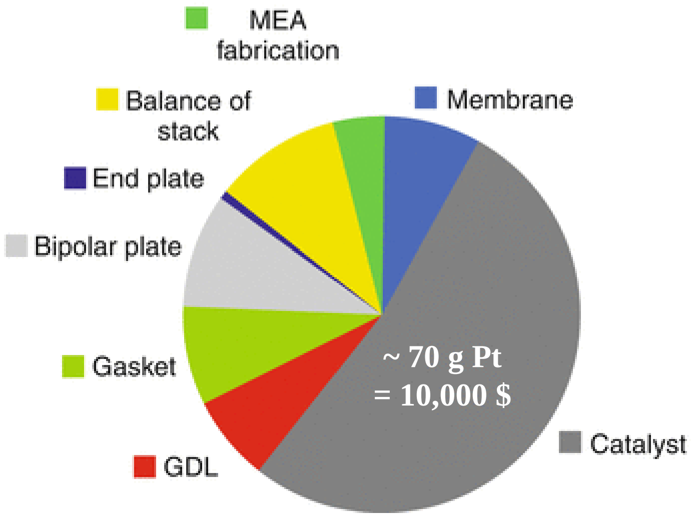
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Nanoparticle Technology

Cost distribution of fuel cell vehicle

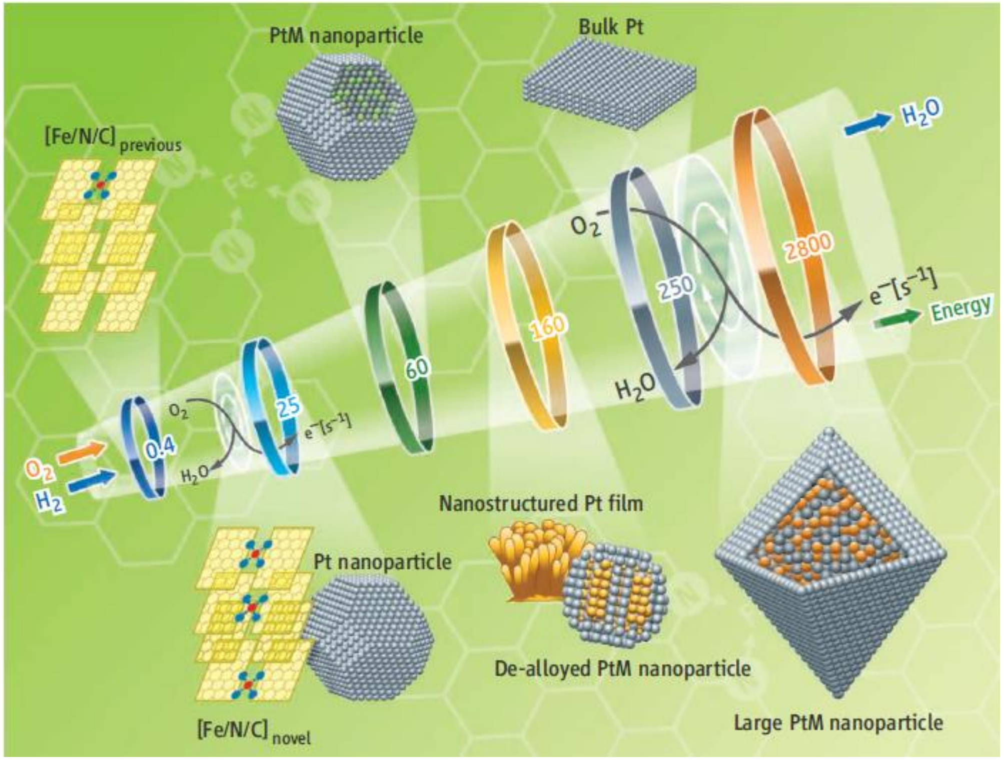




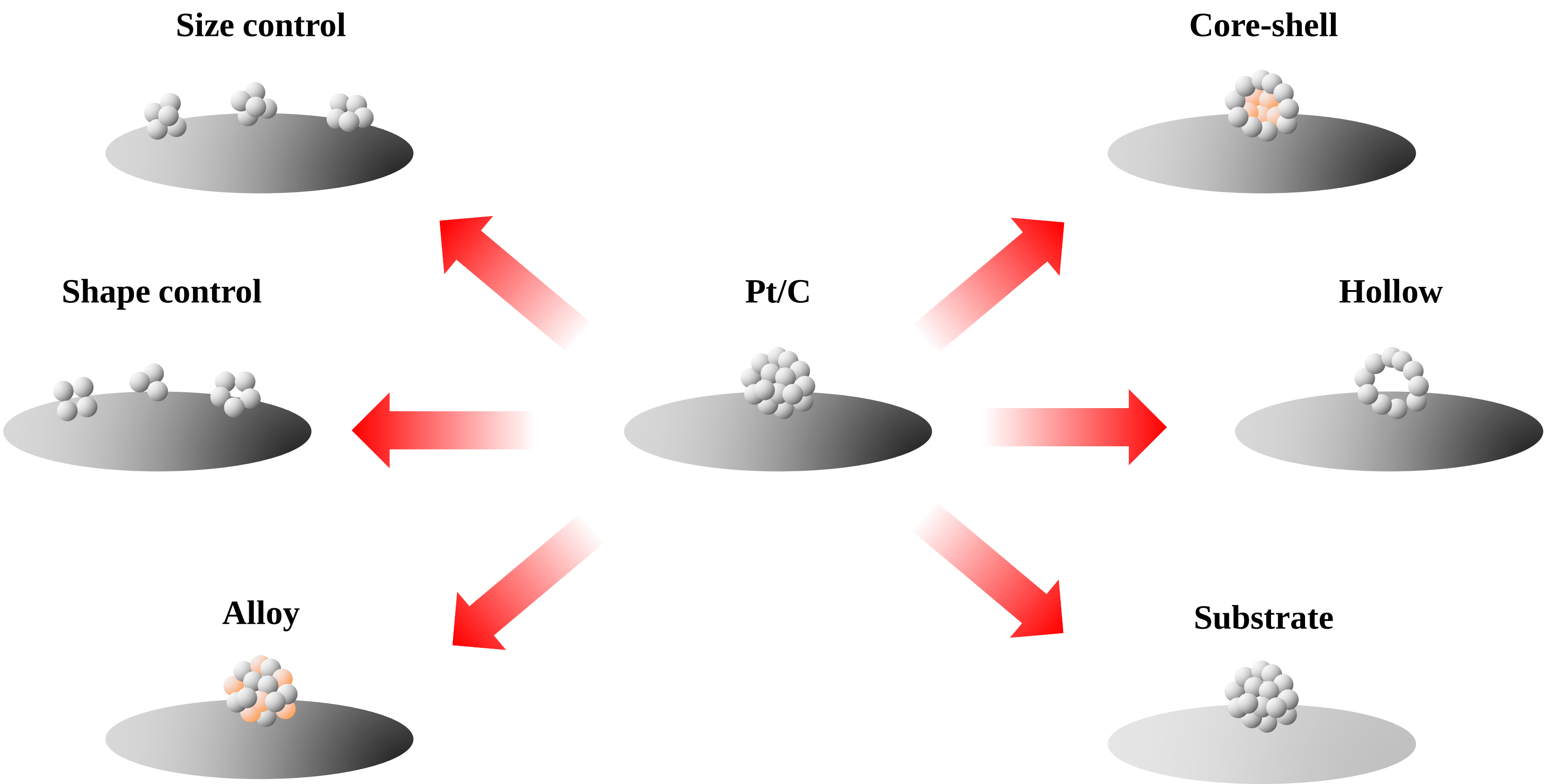


Nanoparticle Technology

Strategies to improve activity of Pt/C



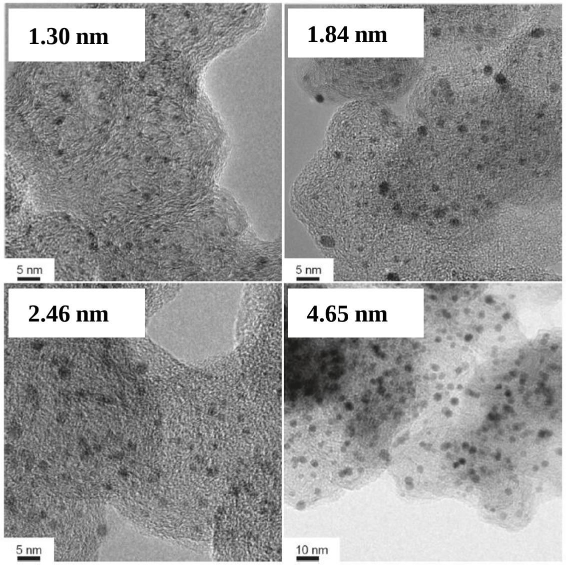
Strategies to improve activity



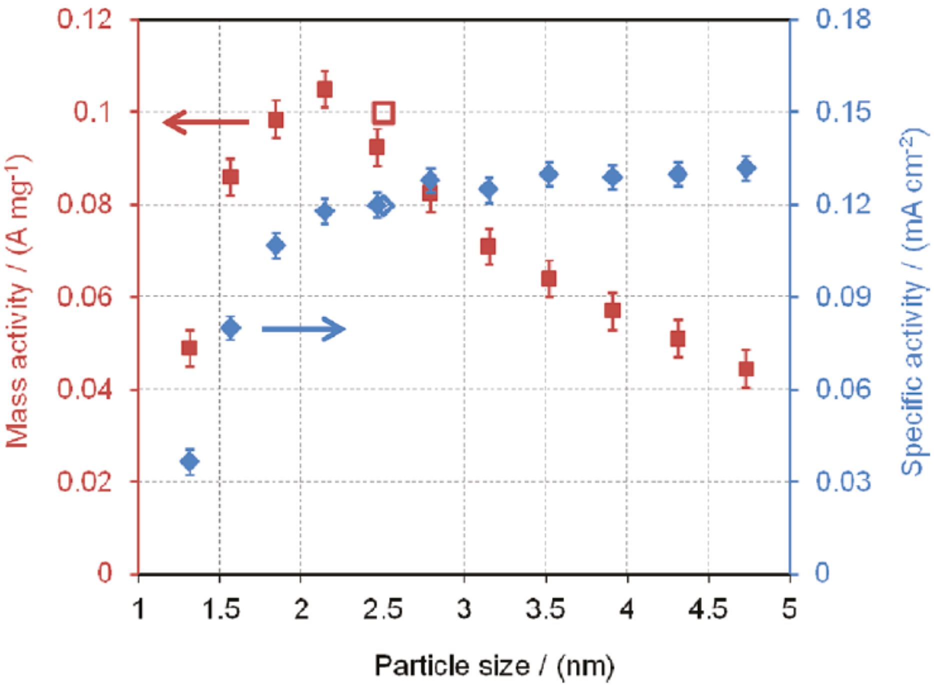
Strategies to improve activity

Size control

TEM images of Pt/C



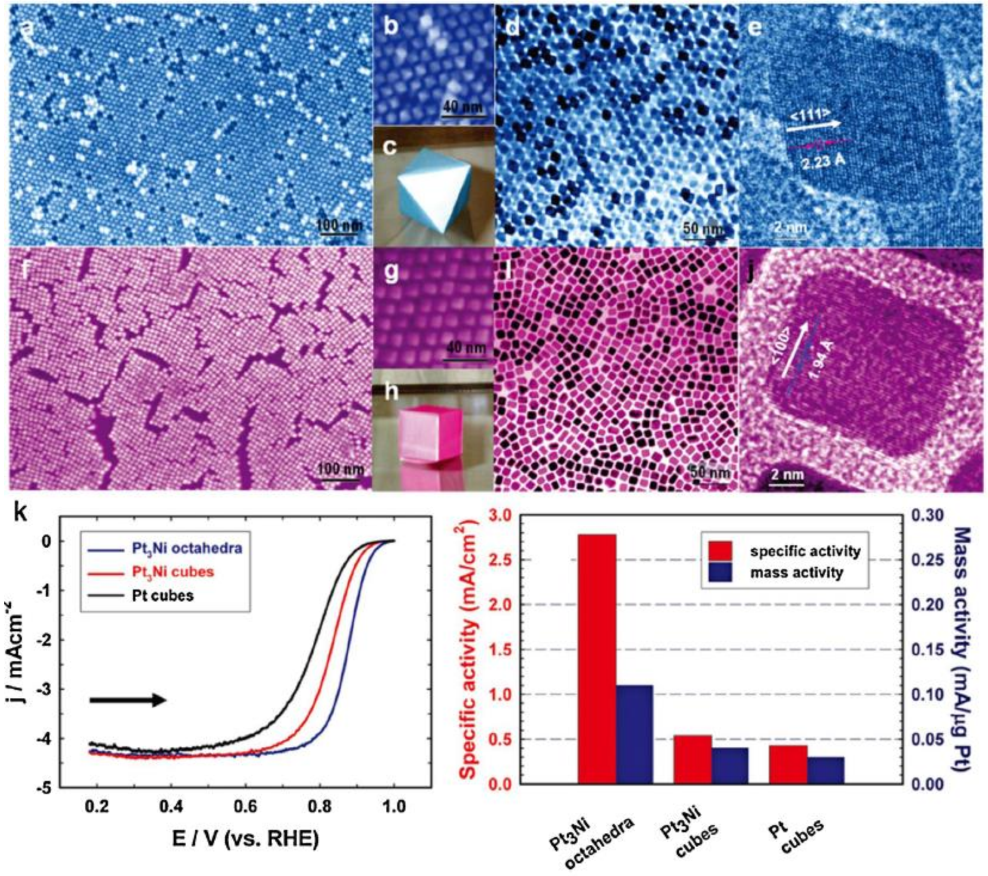
Oxygen reduction reaction at 0.93 V_{RHE}



[Nano Lett. 11 (2011) 3714.]

Strategies to improve activity

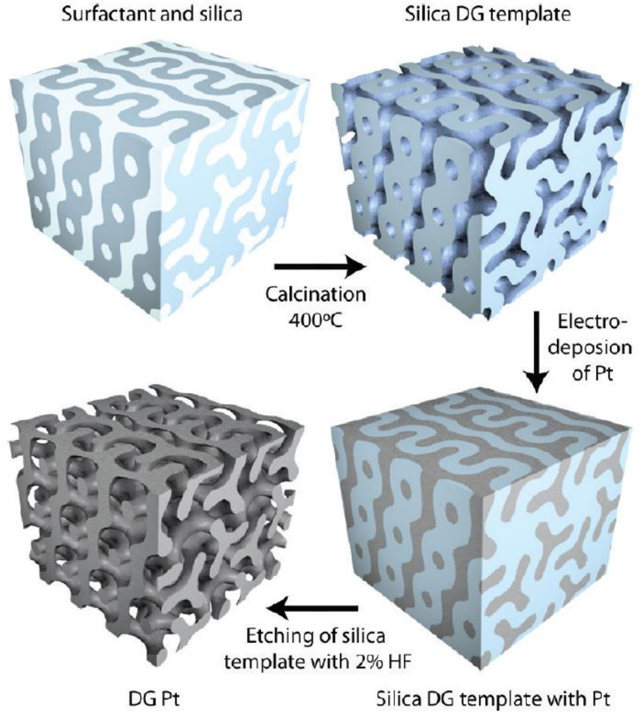
Shape control



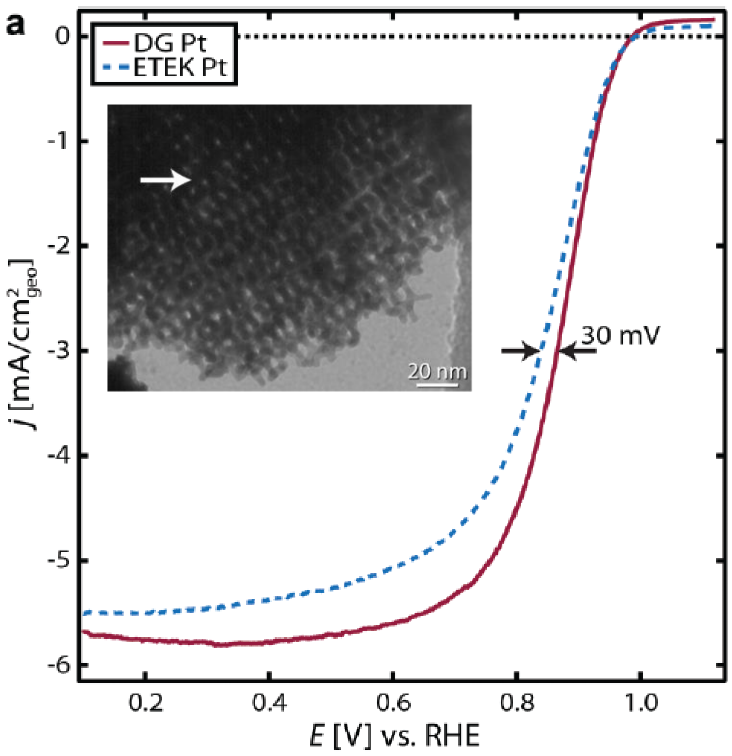
[Nano Lett. 10 (2010) 638.]

Strategies to improve activity

Shape control



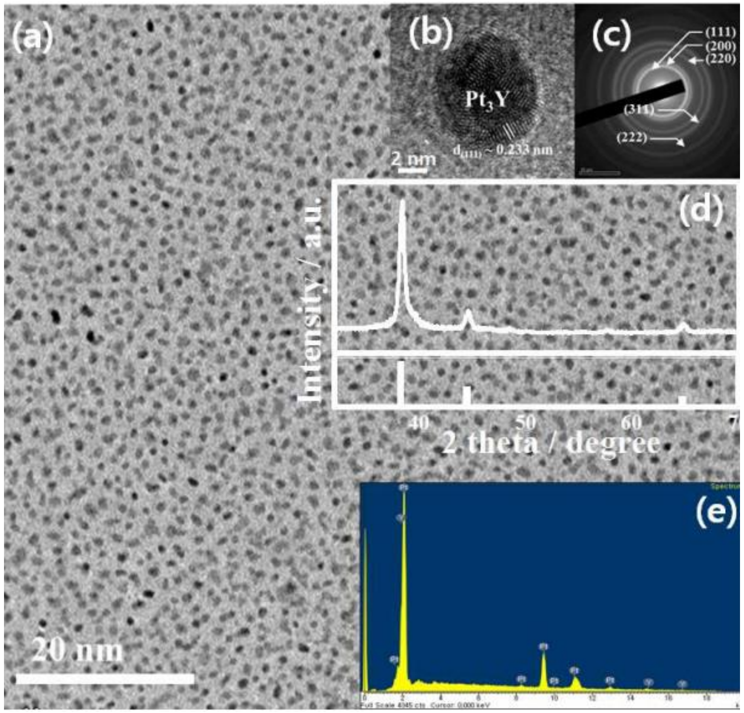
Double gyroid (DG)

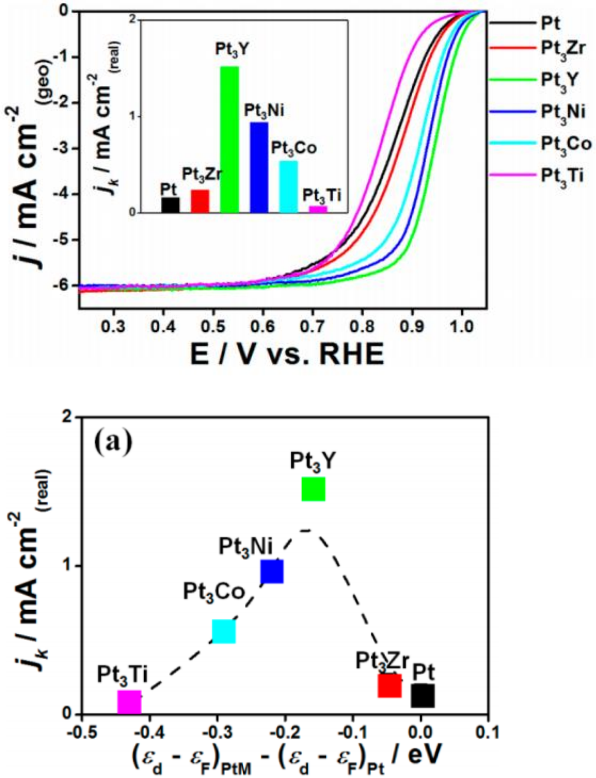


[J. Am. Chem. Soc. 134 (2012) 7758.]

Strategies to improve activity

Alloy

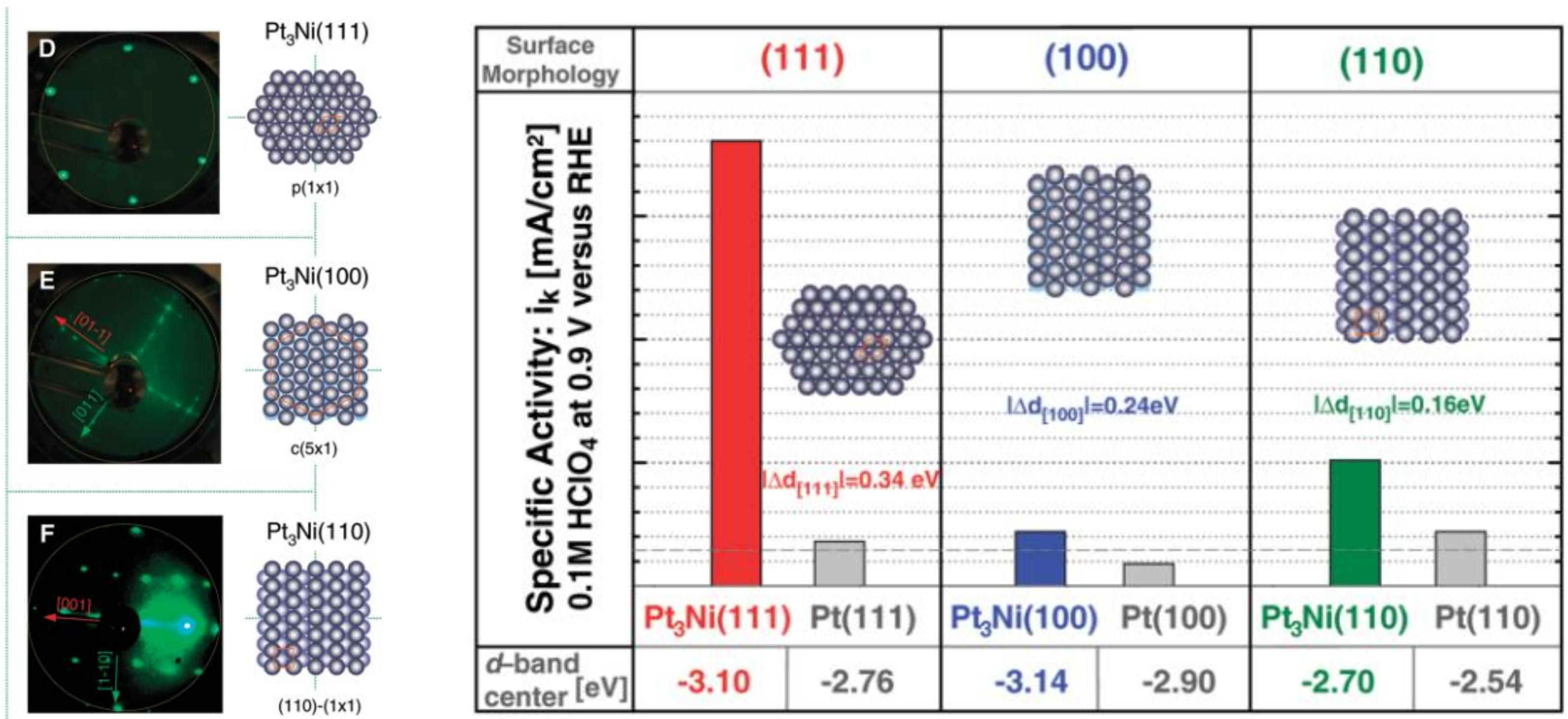




[J. Am. Chem. Soc. 134 (2012) 19508.]

Strategies to improve activity

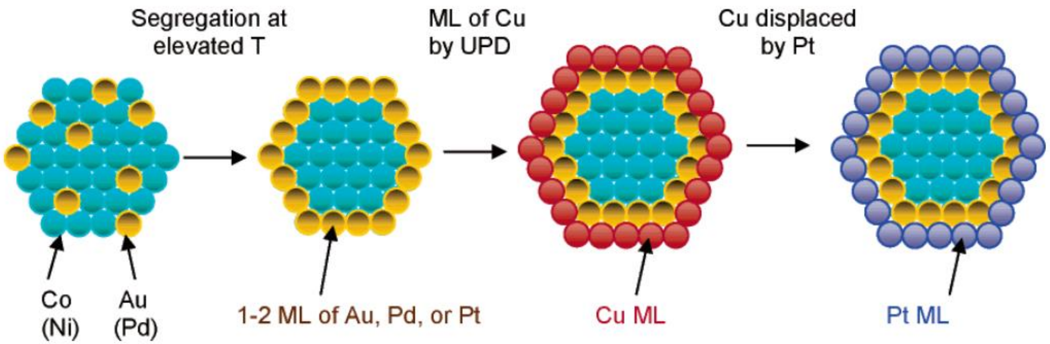
Alloy

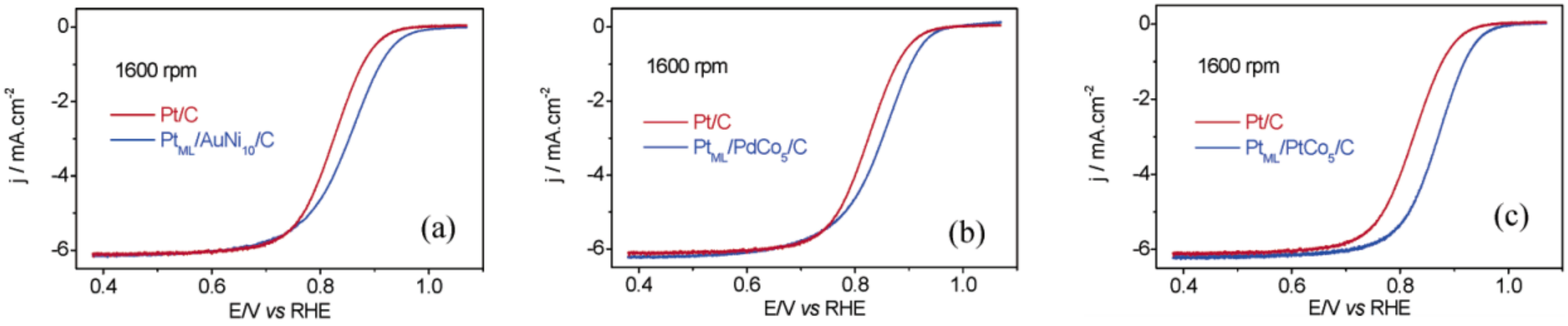


[Science 315 (2007) 493.]

Strategies to improve activity

Core-shell

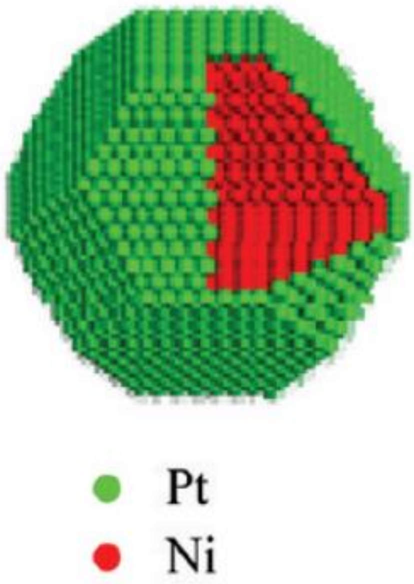


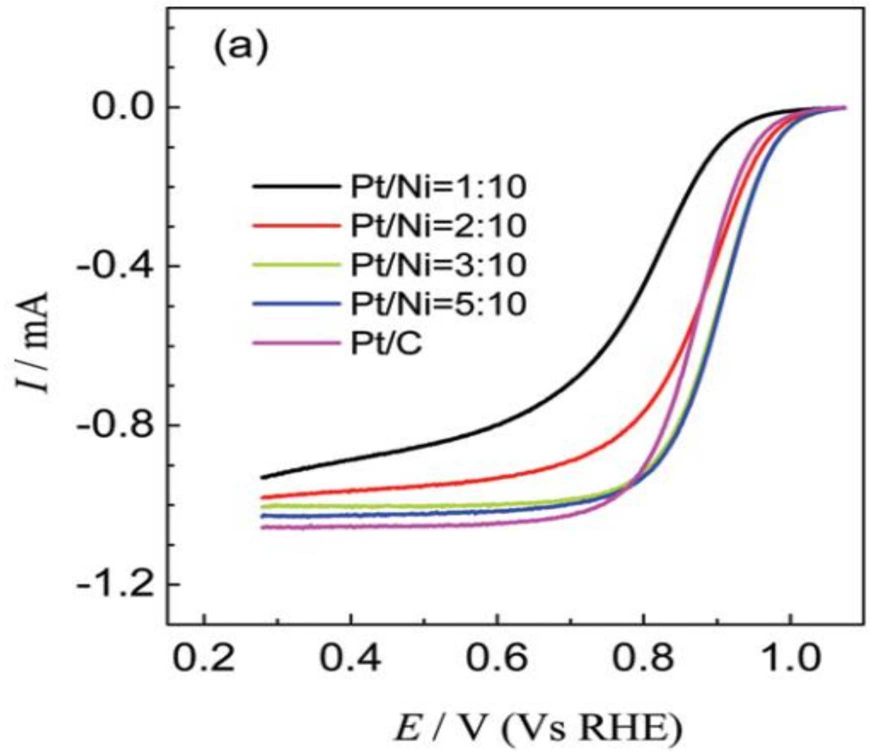


[J. Phys. Chem. B 109 (2005) 22701.]

Strategies to improve activity

Core-shell

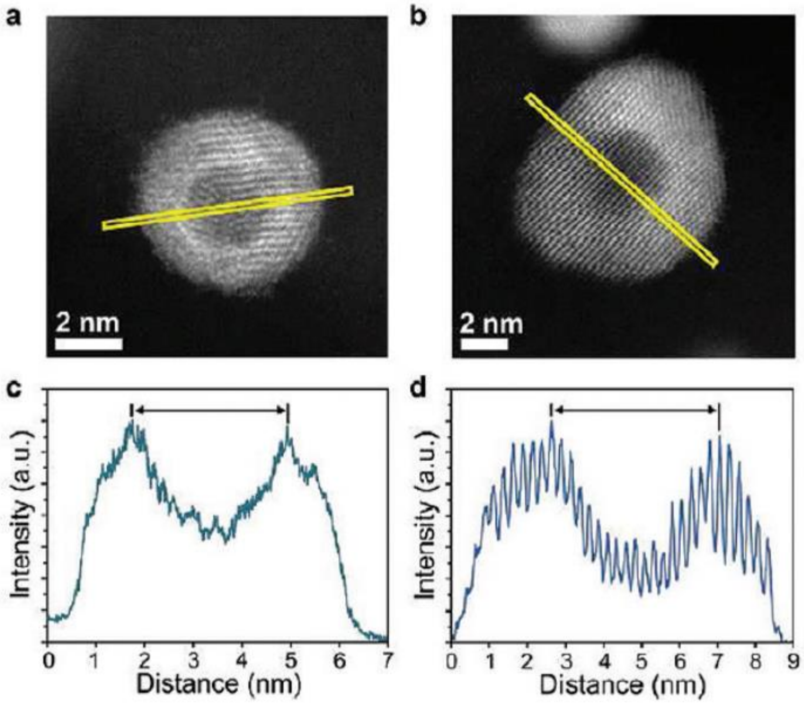


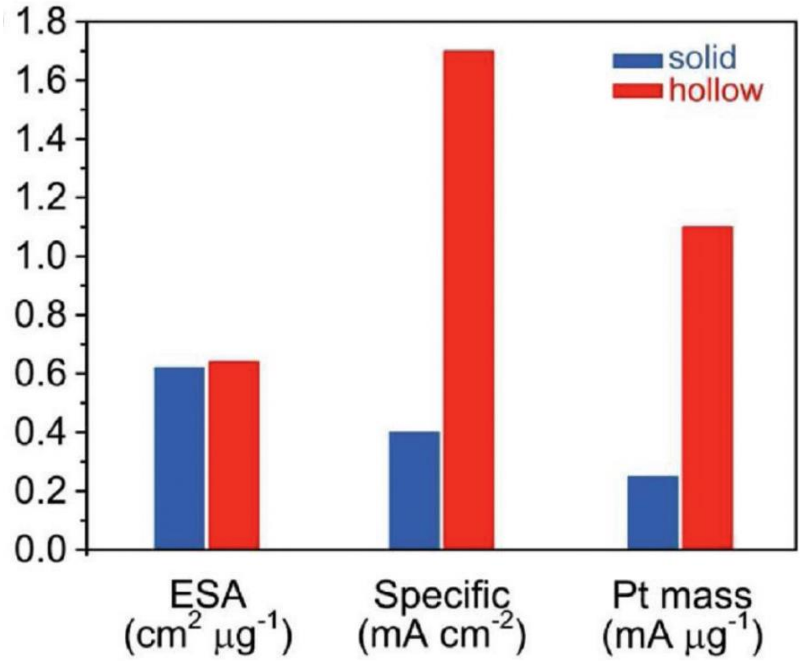


[J. Phys. Chem. C 115 (2011) 24073.]

Strategies to improve activity

Hollow



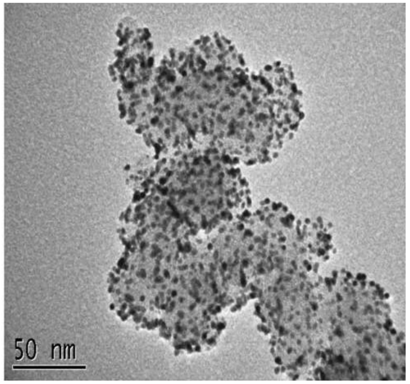


[J. Am. Chem. Soc. 133 (2011) 13551.]

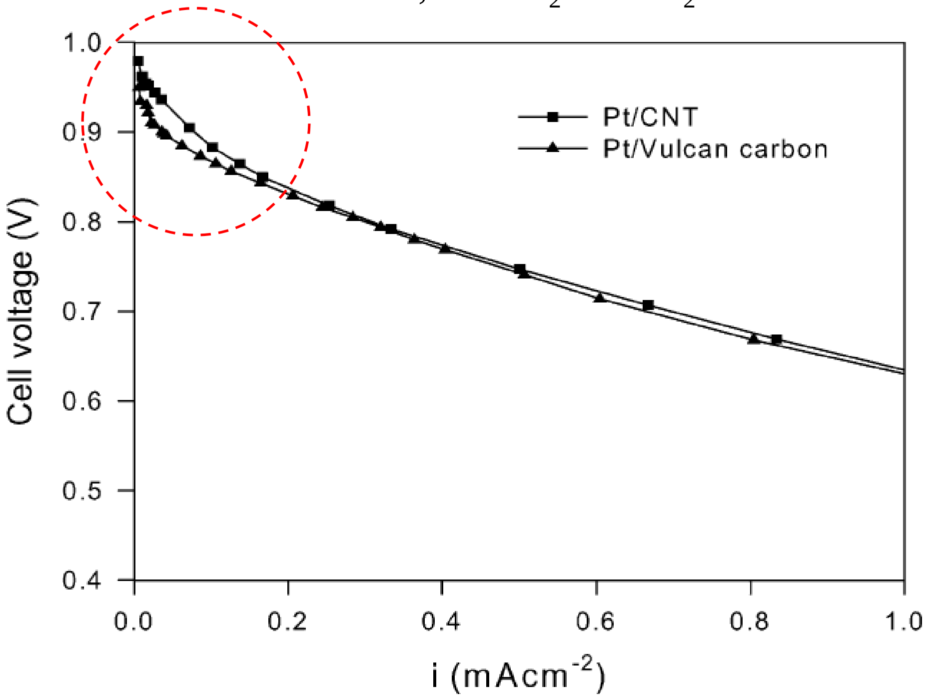
Strategies to improve activity

Substrate

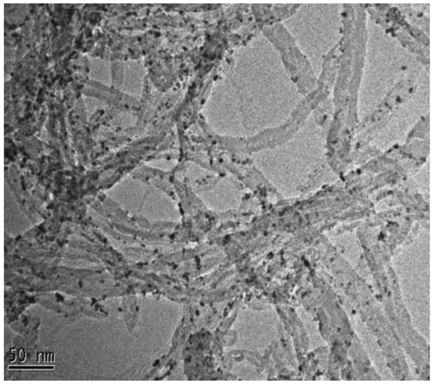
Pt/C



50 °C, 1 bar H_2/1 bar O_2



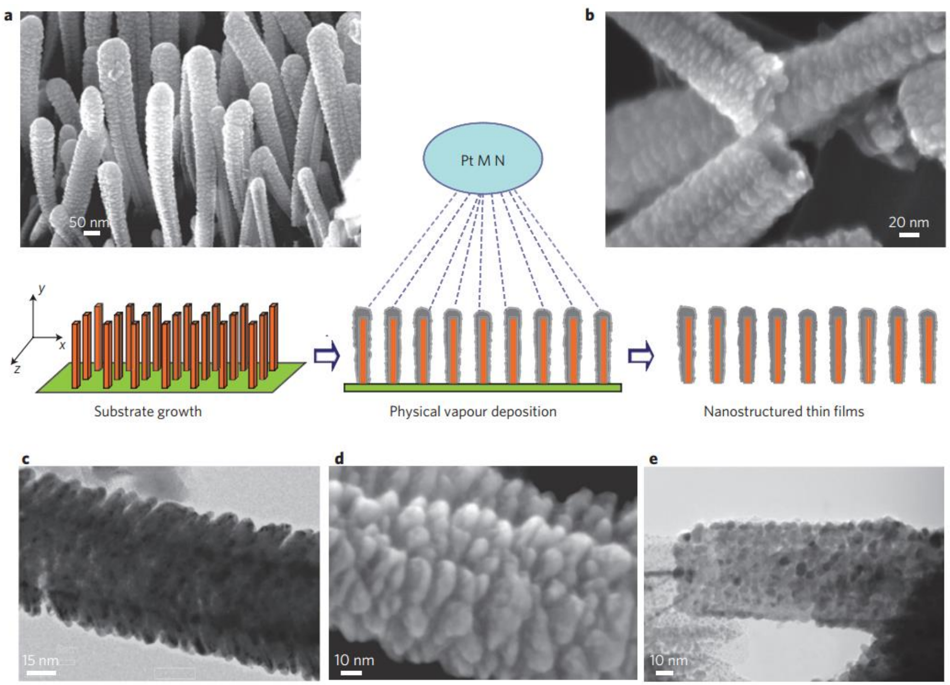
Pt/CNT

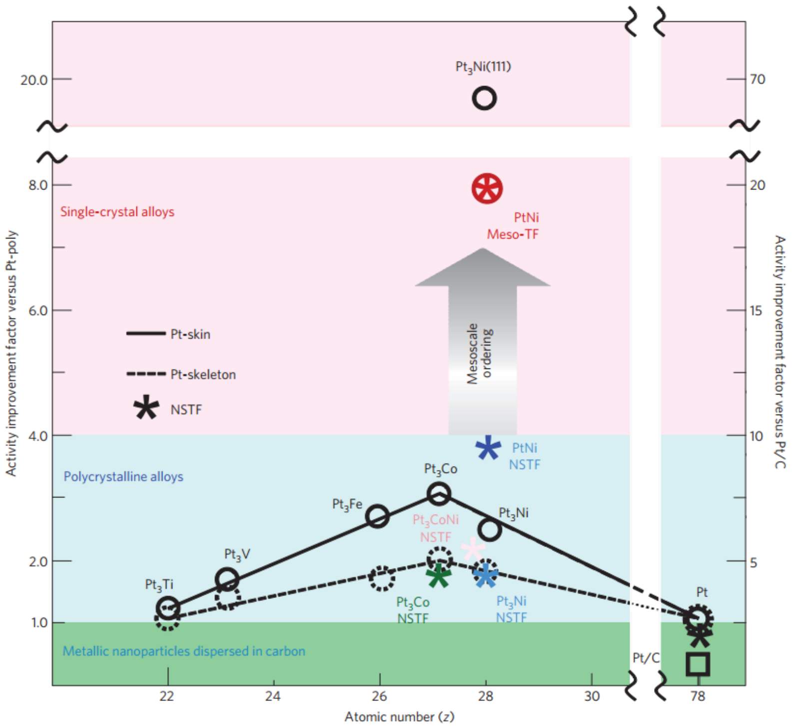


[J. Power Sources 139 (2005) 73.]

Strategies to improve activity

Substrate



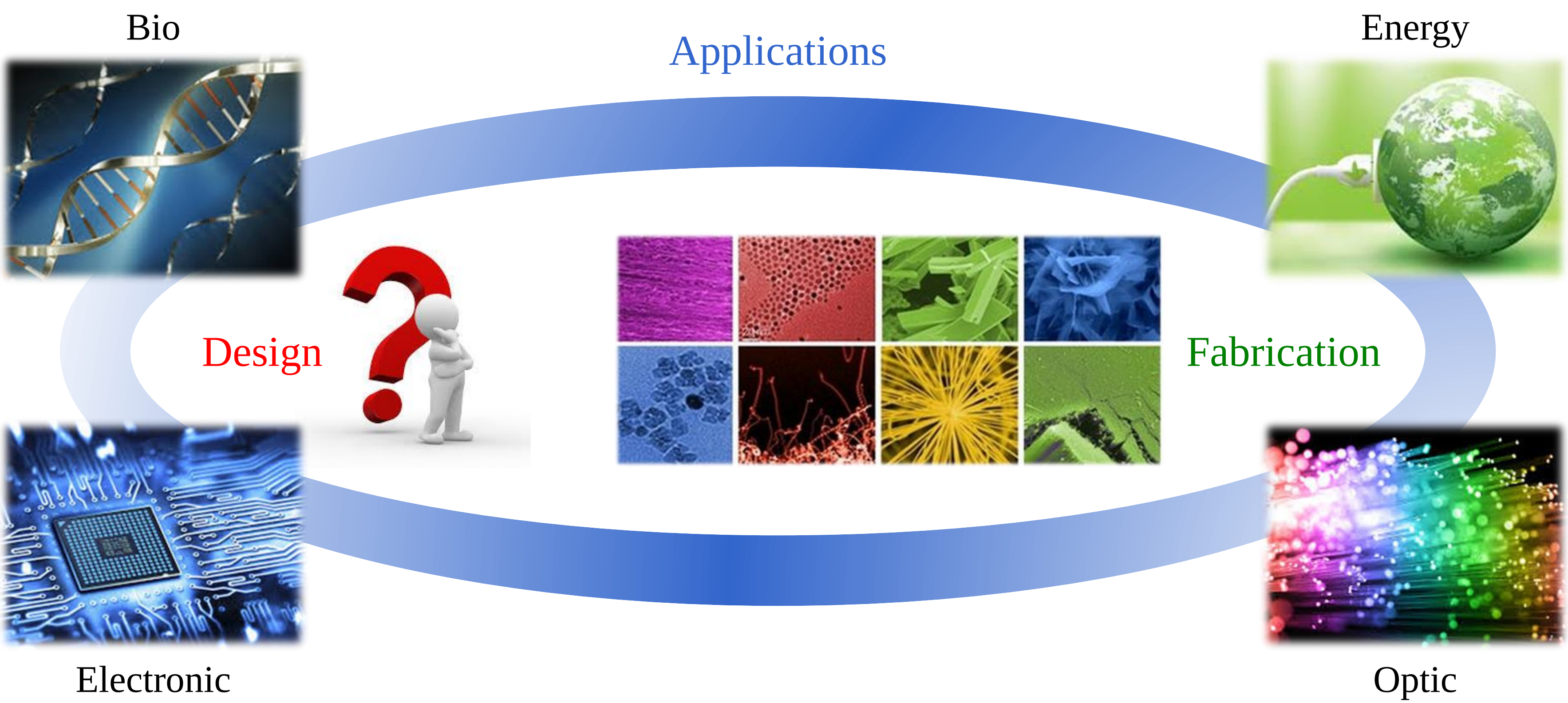


[Nat. Mater. 11 (2012) 1051.]

Nanoparticle Technology

What is nanotechnology?

- In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials.



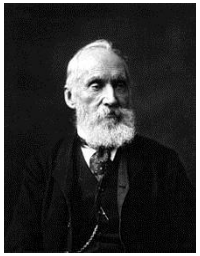
Introduction to Energy Engineering

Energy: definition

Word "energy" is originated from the Ancient Greek "energeia" meaning activity and operation.

Thomas Young

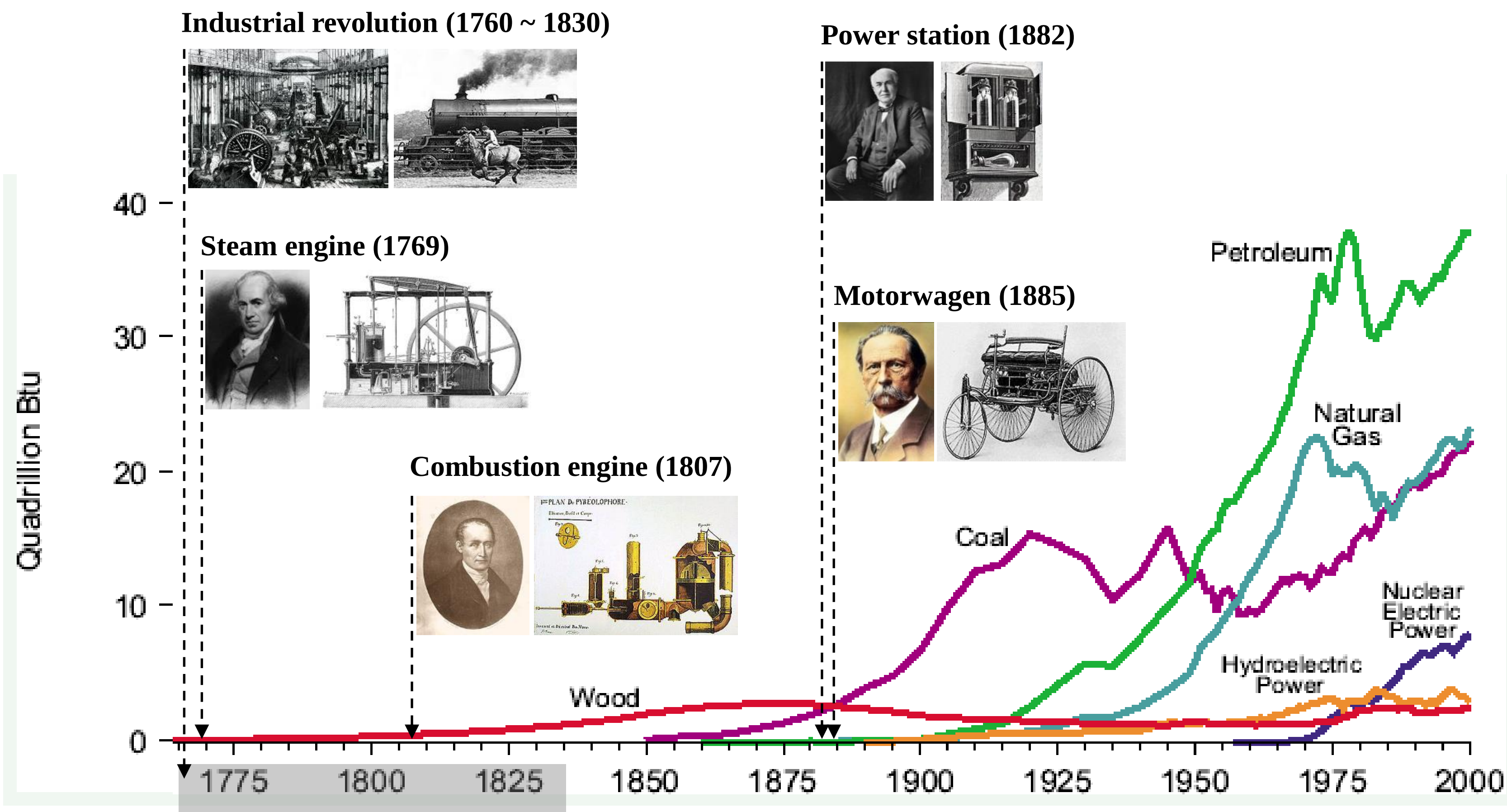
In 1807,
Thomas Young firstly used scientific word "energy" in modern sense.



William Thomson (Lord Kelvin)

In 1852,
William Thomson introduced the energy to thermodynamics with the theory of conservation of energy (first law of thermodynamics).

Energy: historical time line



Forms of Energy

Mechanical

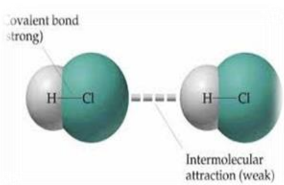
Potential

Mechanical wave

Kinetic

Nuclear

Chemical



Thermal (heat)

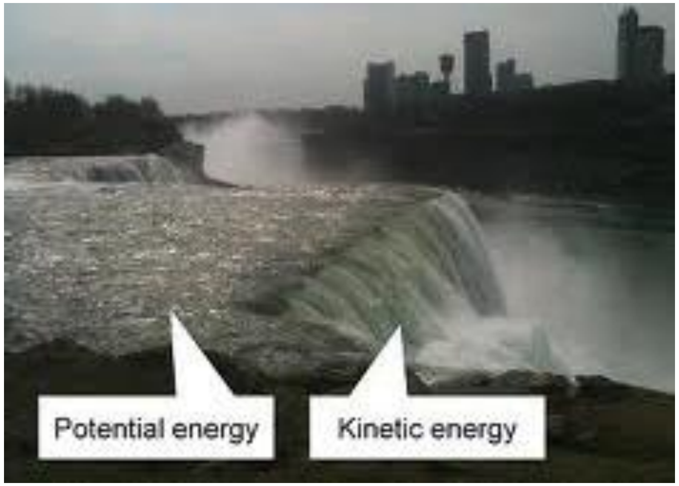
Electrical

Radiant

Magnetic

Energy classification 1: thermodynamics

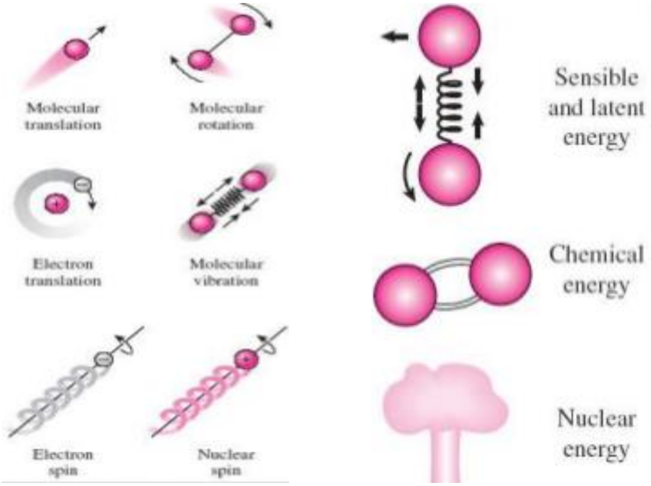
Macroscopic energy



Potential energy (*PE*):
The energy that a system possesses as a result of its **elevation in a gravitational field**.

Kinetic energy (*KE*):
The energy that a system possesses as a result of its **motion relative to some reference frame**.

Microscopic energy

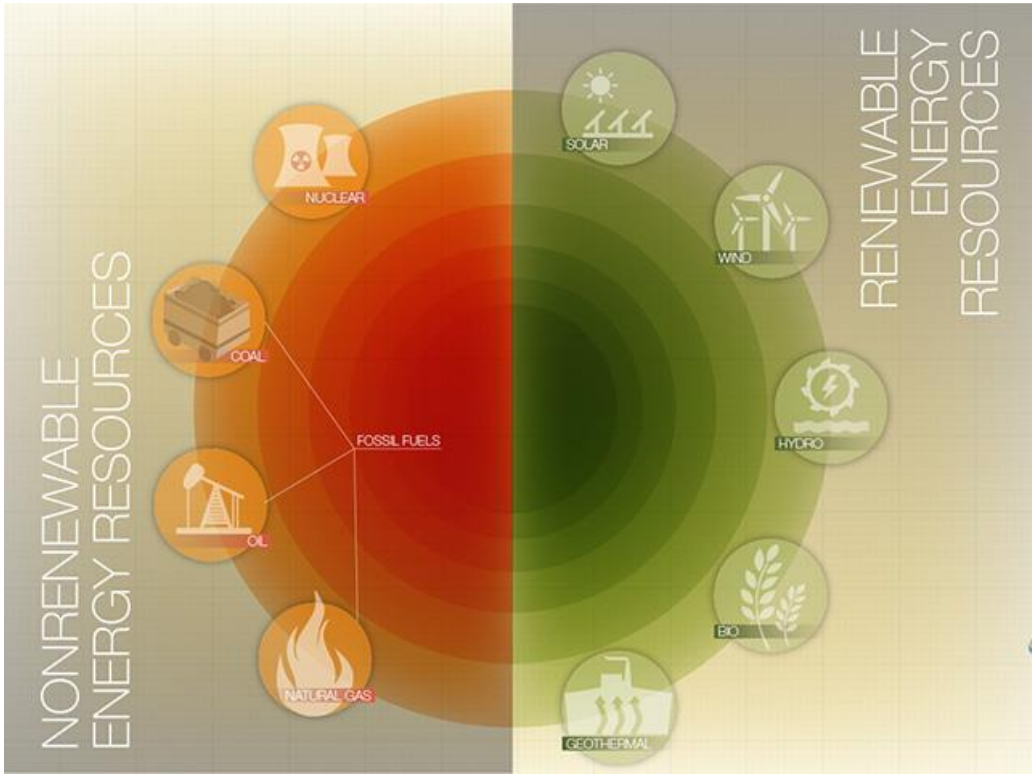


Internal energy (*U*):
Sum of all microscopic forms of energy

Total energy of a system: $E = PE + KE + U$

Energy classification 2: renewablility

Non-renewable energy | **Renewable energy**



Energy classification 3: use stage

Primary energy (sources) → **Secondary energy (refined or generated)** → **Final energy (beneficial for real life)**

Primary energy (sources)



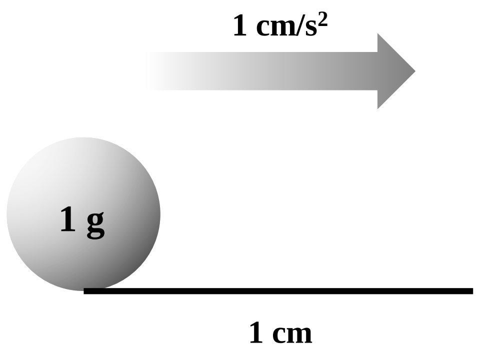



Secondary energy (refined or generated)

Final energy (beneficial for real life)



Energy units



$$1\ \text{g} \times 1\ \text{cm} \times 1\ \text{cm/s}^2 = 1\ \text{erg} = 10^{-7}\ \text{J (Joule)}$$

$$1\ \text{J} = 2.39 \times 10\ \text{cal} = 2.78 \times 10^{4}\ \text{W·h} = 6.24 \times 10^{18}\ \text{eV} = 2.39 \times 10^{-4}\ \text{g TNT}$$

Thermal (heat)

Food industry

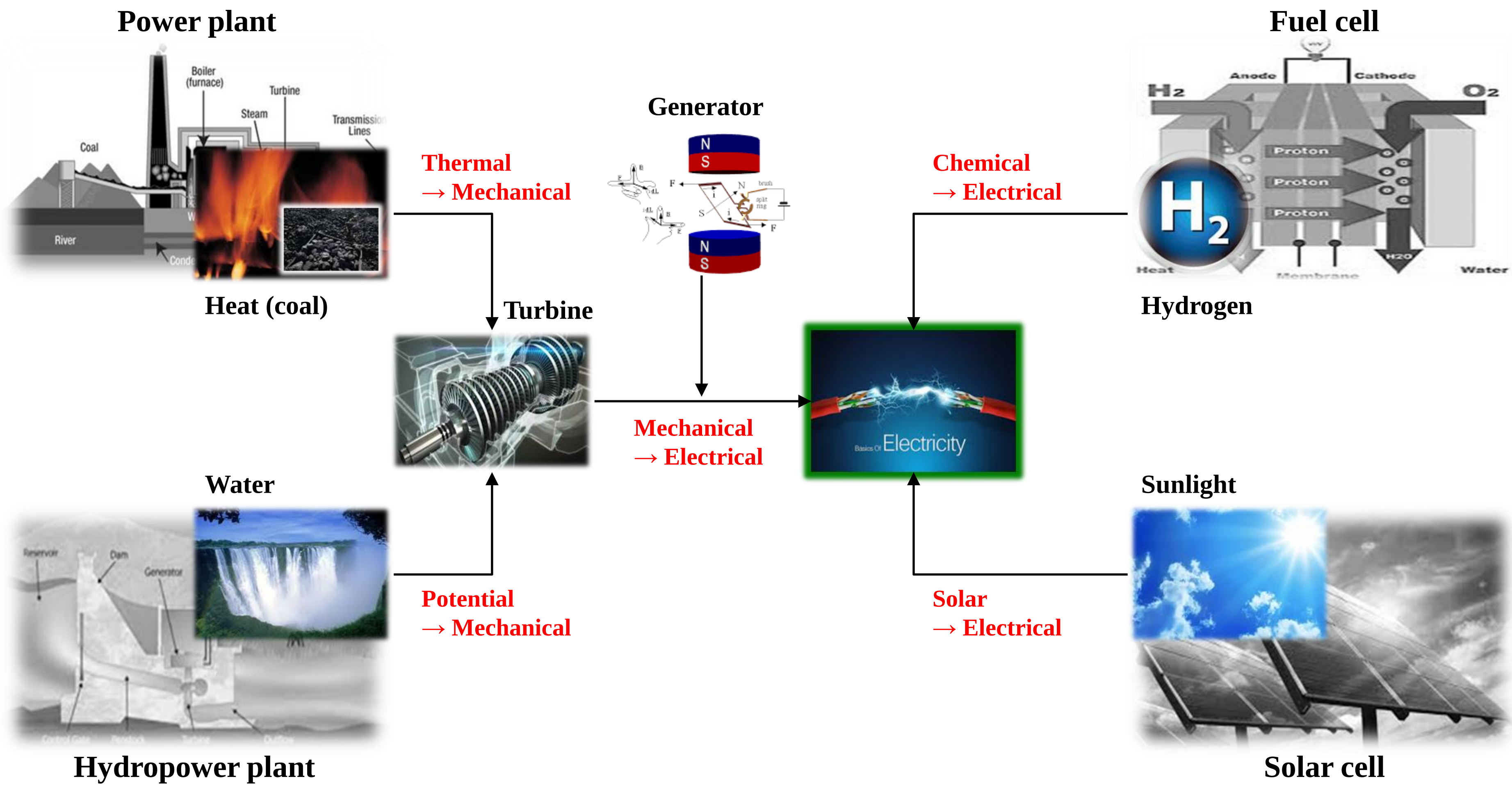
Power

Electrical

Explosive

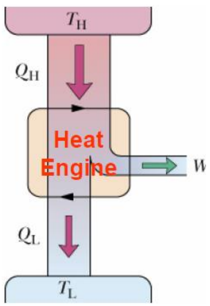
Nanoparticle Technology

Energy conversion for electricity

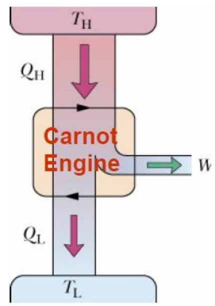


Energy issues: 1. Conversion efficiency

Power plant



Ideal heat engine
1. No friction
2. ΔS = Q/T = 0
3. Reversible



Efficiency at T_H = 673 K (400 °C) and T_L = 298 K (25 °C)

$$\varepsilon = \frac{Useful\ output}{Total\ input} = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H} = 0.56$$

$$|W| = |Q_H| - |Q_L|$$

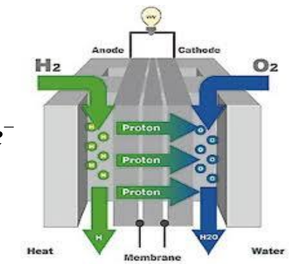
1st law: conservation of energy

$$\Delta S = 0 = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

$$\rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

Fuel cell

$$H_2 \rightarrow 2H^+ + 2e^-$$



$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$H_2 + 0.5O_2 \leftrightarrow H_2O$$

Ideal fuel cell
Reversible

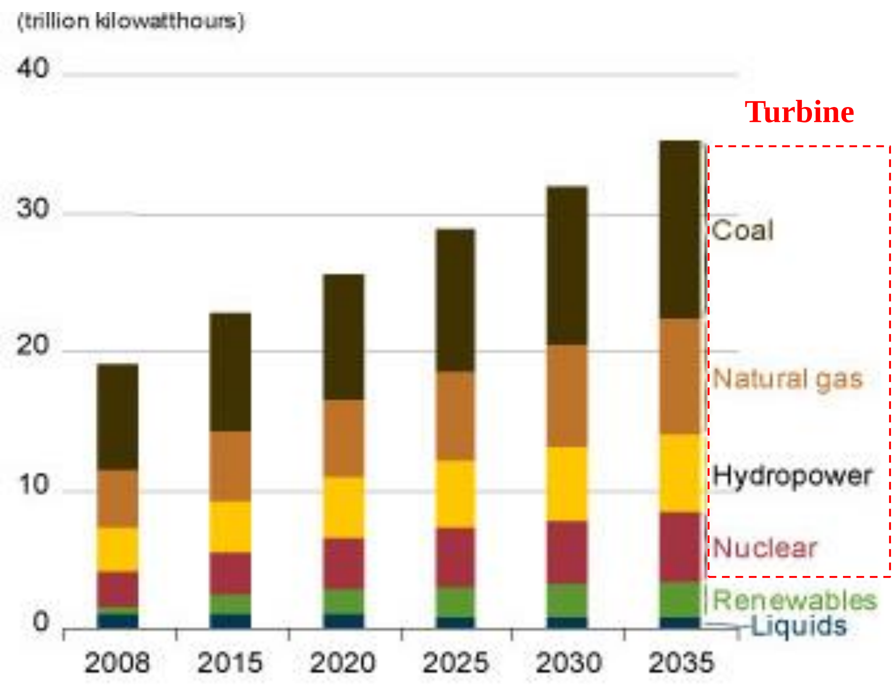
Efficiency at 298 K (25 °C)

$$\varepsilon = \frac{Useful\ output}{Total\ input} = \frac{\Delta G^0_{298K}}{\Delta H^0_{298K}} = \frac{-237\ kJ/mol}{-286\ kJ/mol} = 0.83$$

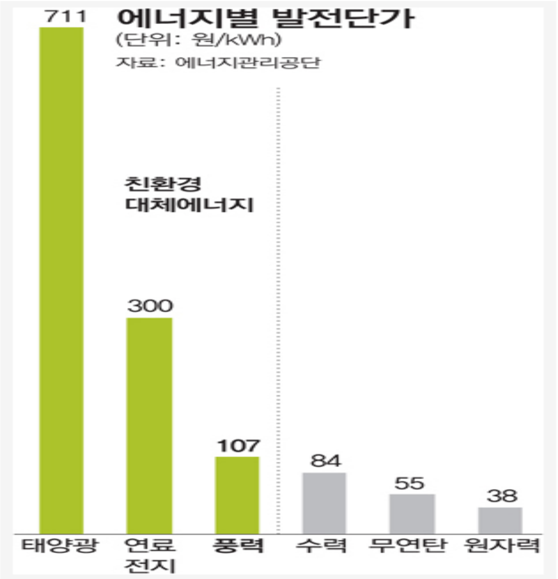
Form of water product	Temp °C	$\Delta \bar{g}_f$, kJ mol^{-1}	Efficiency limit %
Liquid	25	−237.2	83
Liquid	80	−228.2	80
Gas	100	−225.2	79
Gas	200	−220.4	77
Gas	400	−210.3	74
Gas	600	−199.6	70
Gas	800	−188.6	66
Gas	1000	−177.4	62

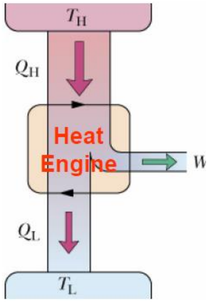
Energy issues: 2. Dependence and cost

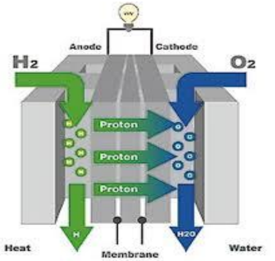
World electricity generation



Source: http://www.eia.gov/forecasts/

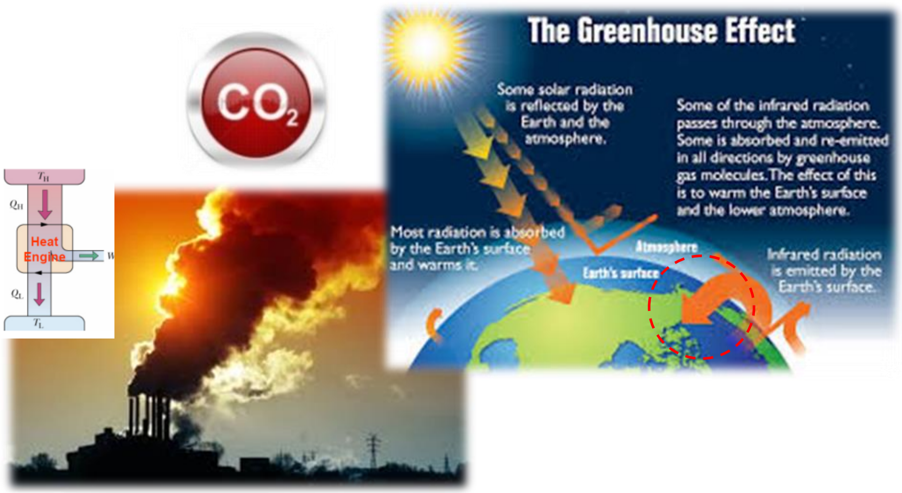




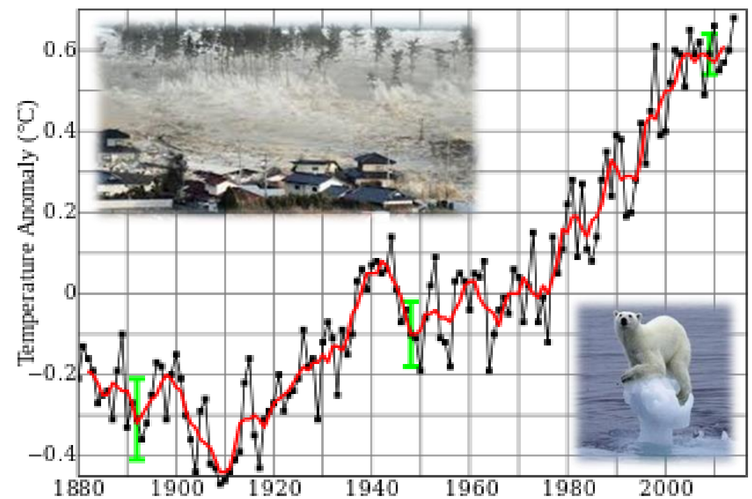


Energy issues: 3. Environment

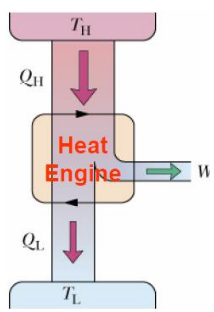
Greenhouse effect

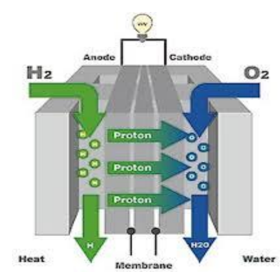


Global warming



$$C + O_2 \rightarrow CO_2$$

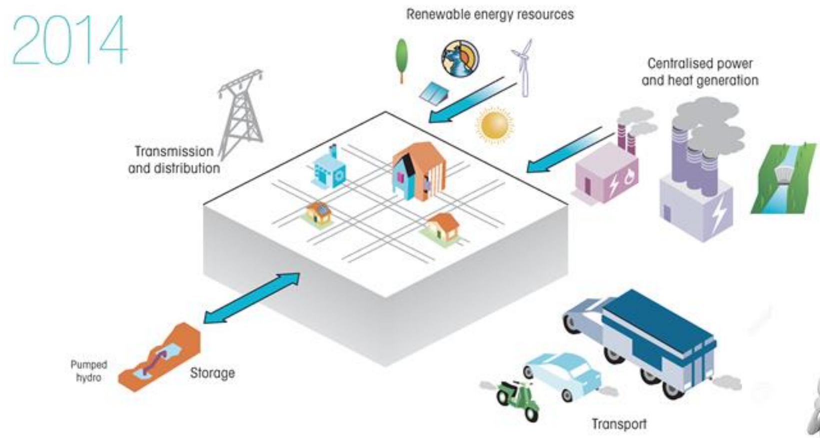


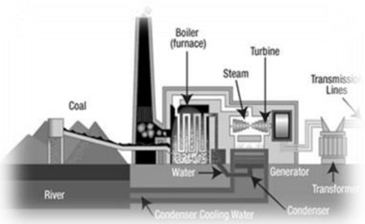


$$H_2 + 0.5O_2 \rightarrow H_2O$$

Nanoparticle Technology

Complementary cooperation for future





Non-renewable energy

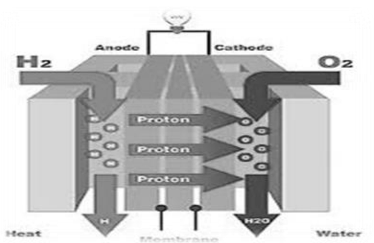
(coal, oil, gas……)

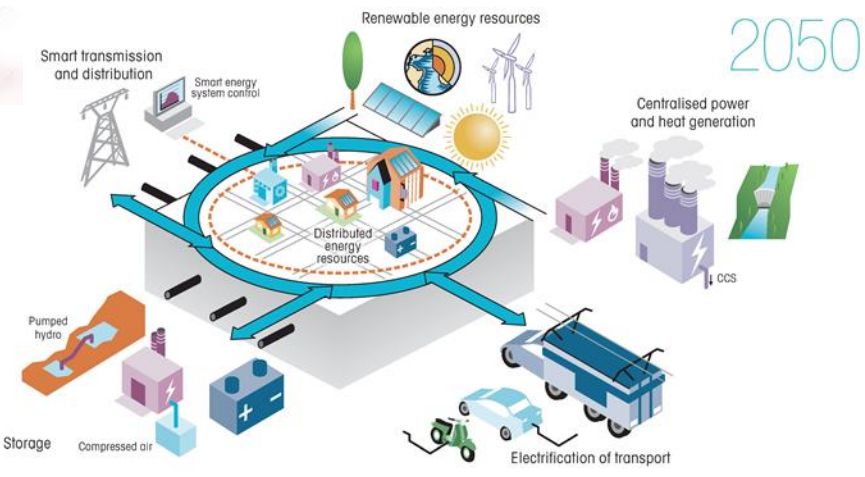
1. **Depletion**
2. **Efficiency**
3. **Environment**

Renewable energy

(sunlight, wind……)

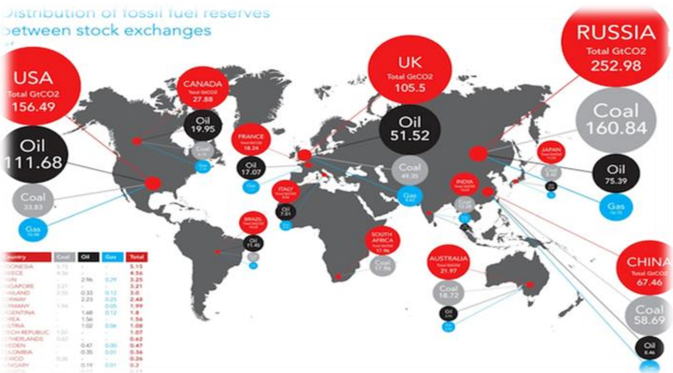
1. **Cost**
2. **Discontinuity**



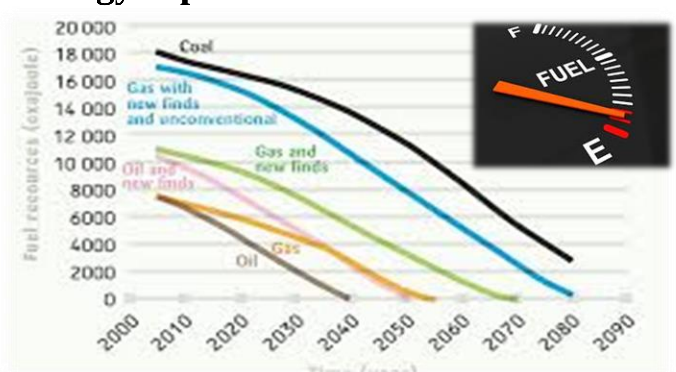


Non-renewable energy for future

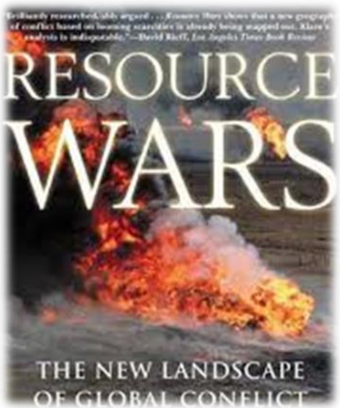
Energy reserves distribution



Energy depletion



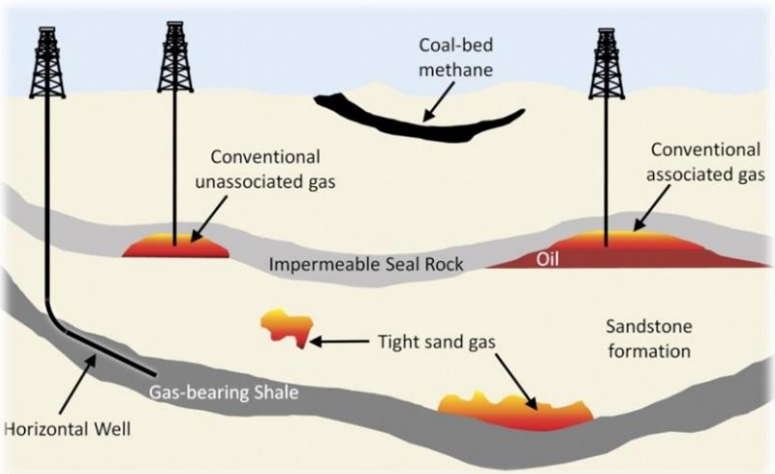
Resources war



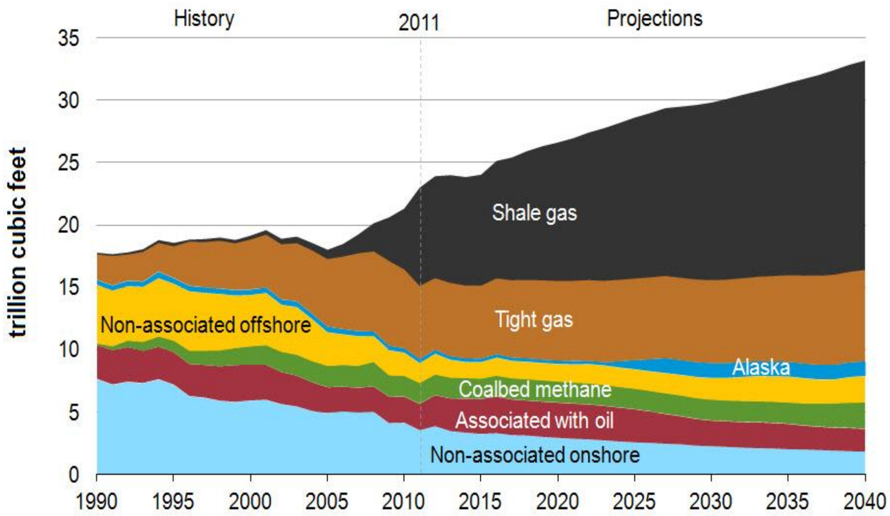
Non-renewable energy for future

Depletion problem (resources explore with advanced technology)

Shale gas



Prediction of gas production portion



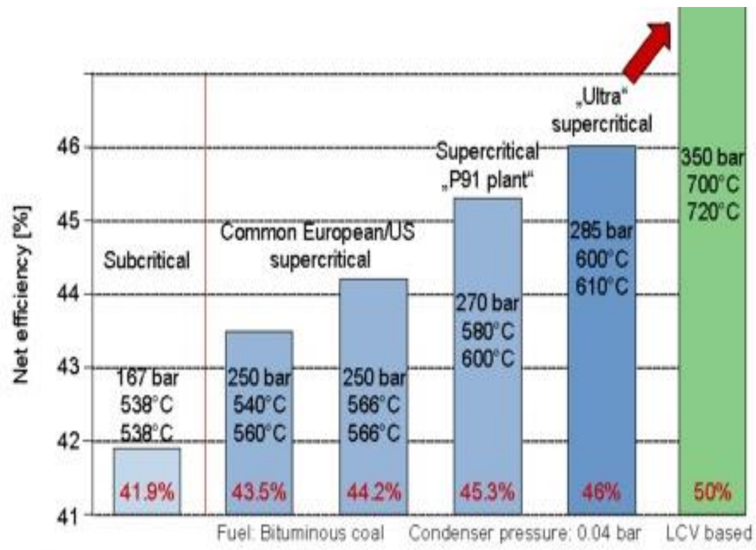
Chemical composition of shale gas is very similar with that of conventional gas.

Production of shale gas will be hugely increased.

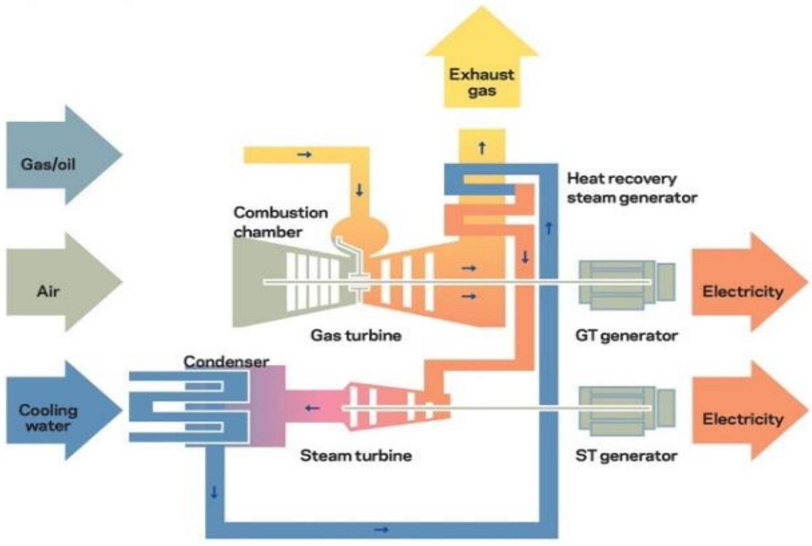
Non-renewable energy for future

Efficiency problem (development of new type power plant)

Ultra-supercritical power plant



Combined cycle power plant

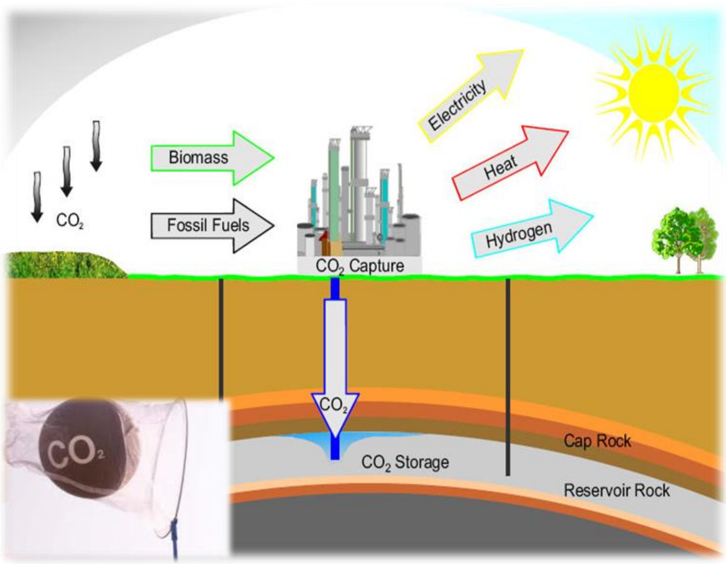


Ultra-supercritical and combined cycle power plants are expected to increase the efficiency compared with conventional power plant.

Non-renewable energy for future

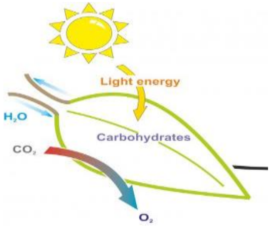
Environment problem

Carbon capture and storage

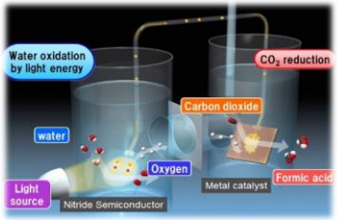


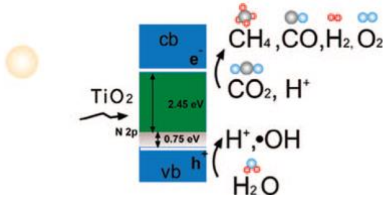
CO_2 conversion (utilization)

Biochemical

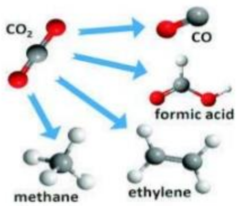


Photochemical





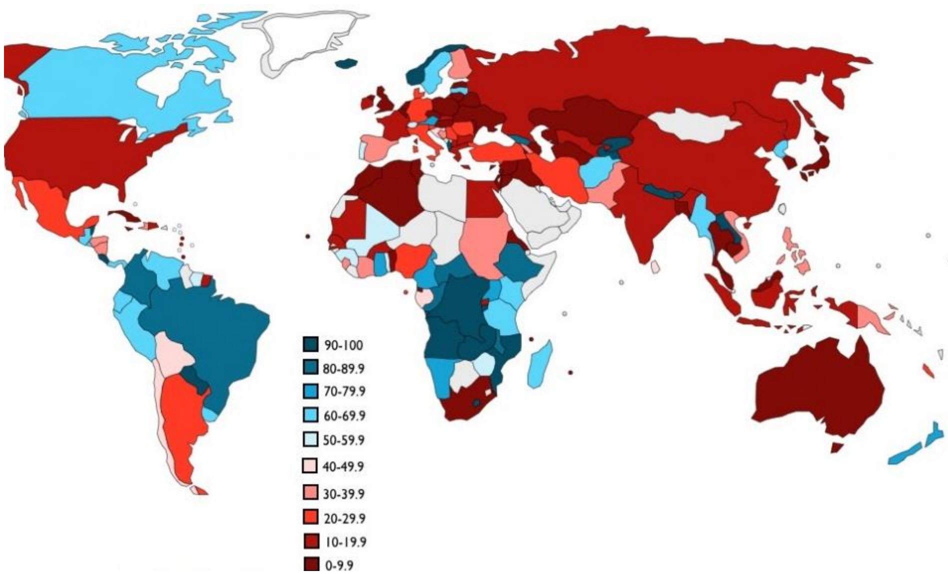
Electrochemical



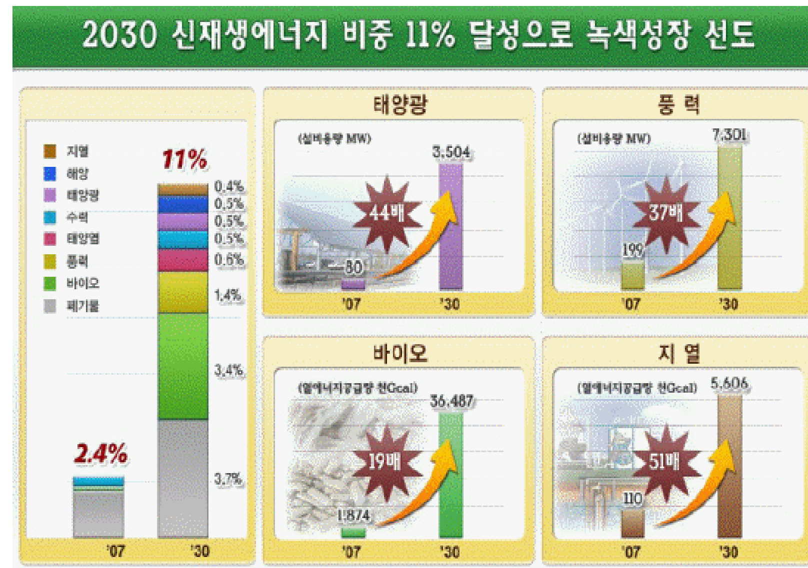
Renewable energy for future

Renewable energy for future

Electricity generation from renewable energy (%)



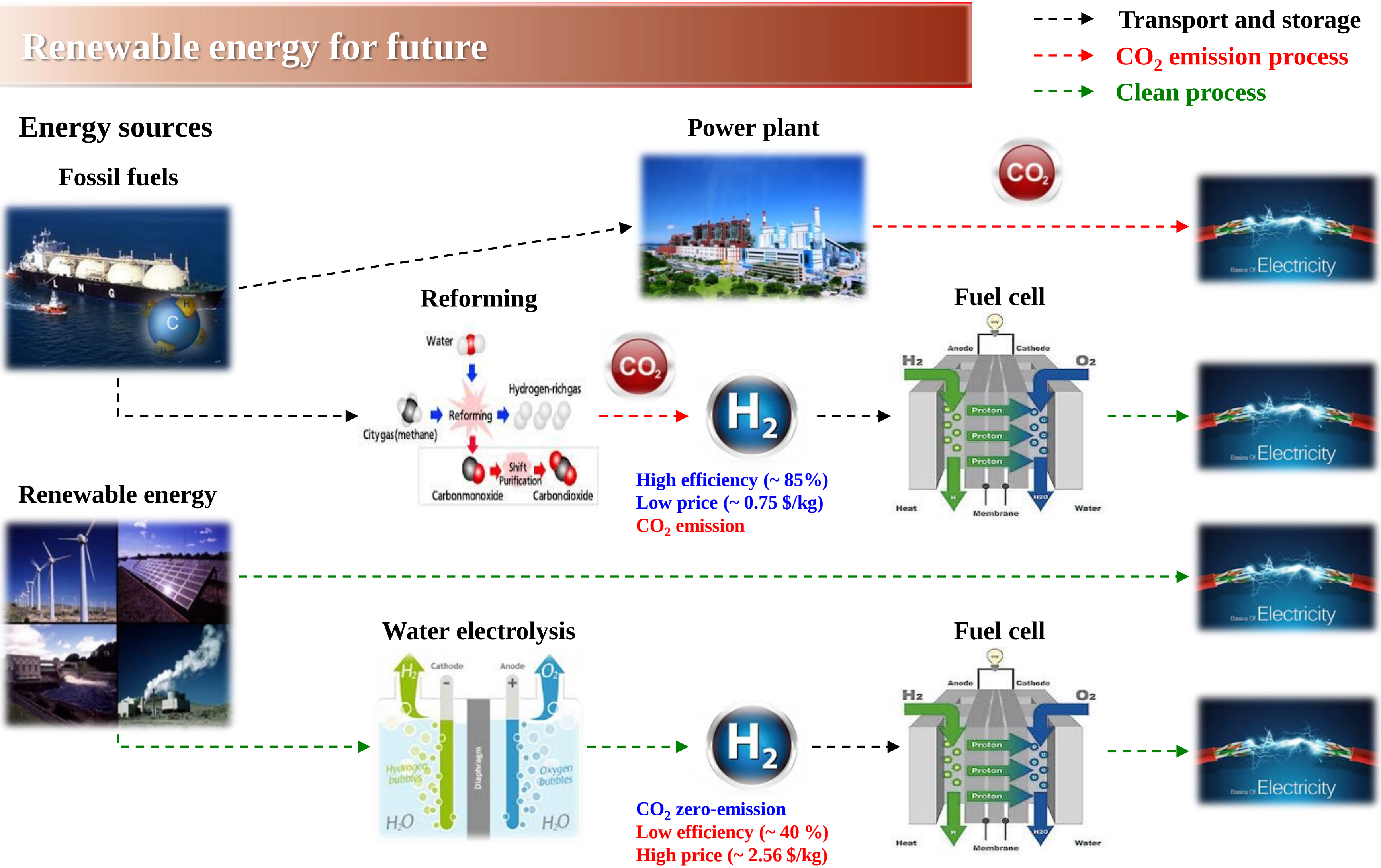
제 1차 국가에너지기본계획 (2008)



In Korea, the electricity generation percentage from renewable energy is below 10 %.

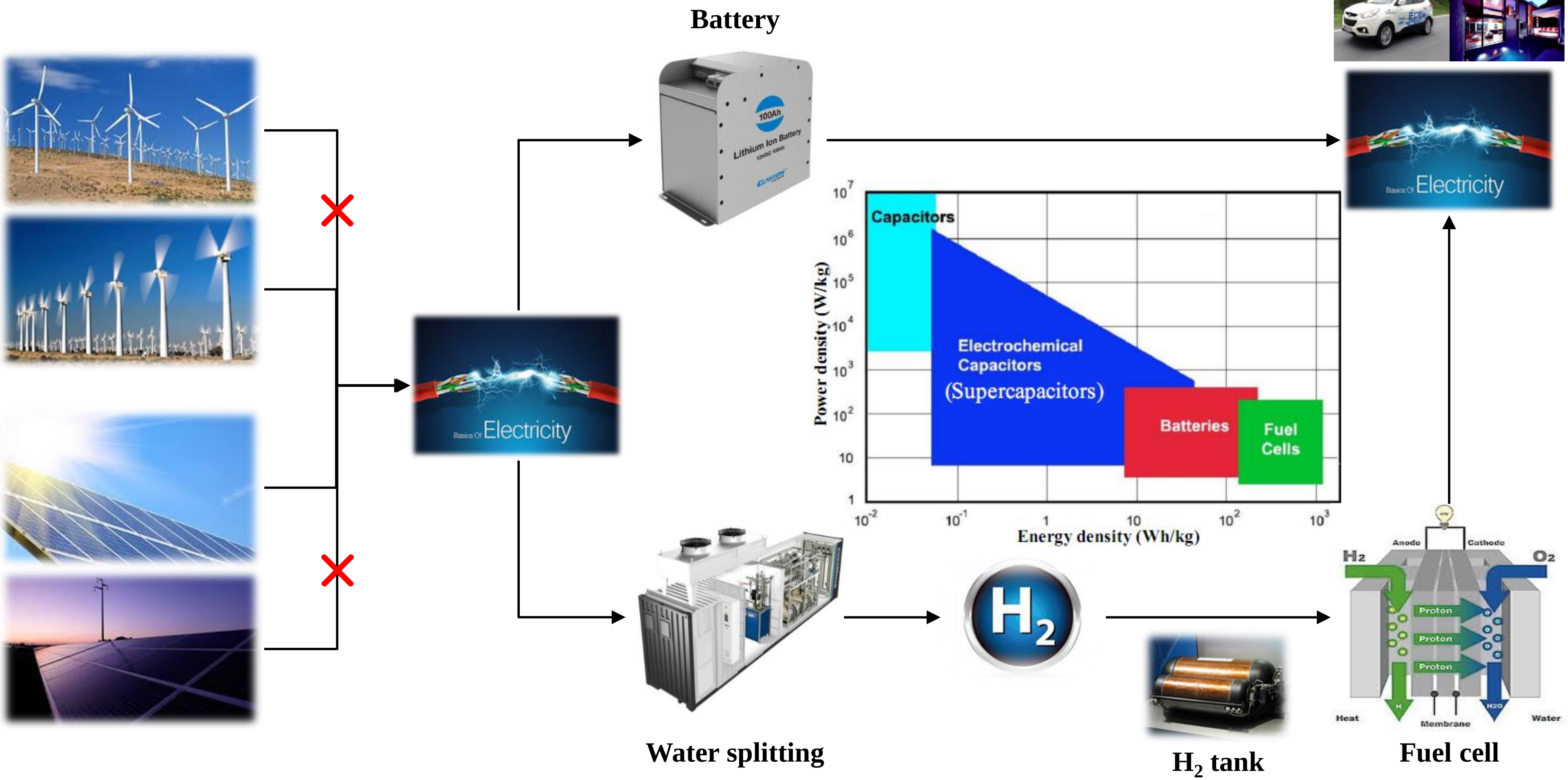
Nanoparticle Technology

Renewable energy for future

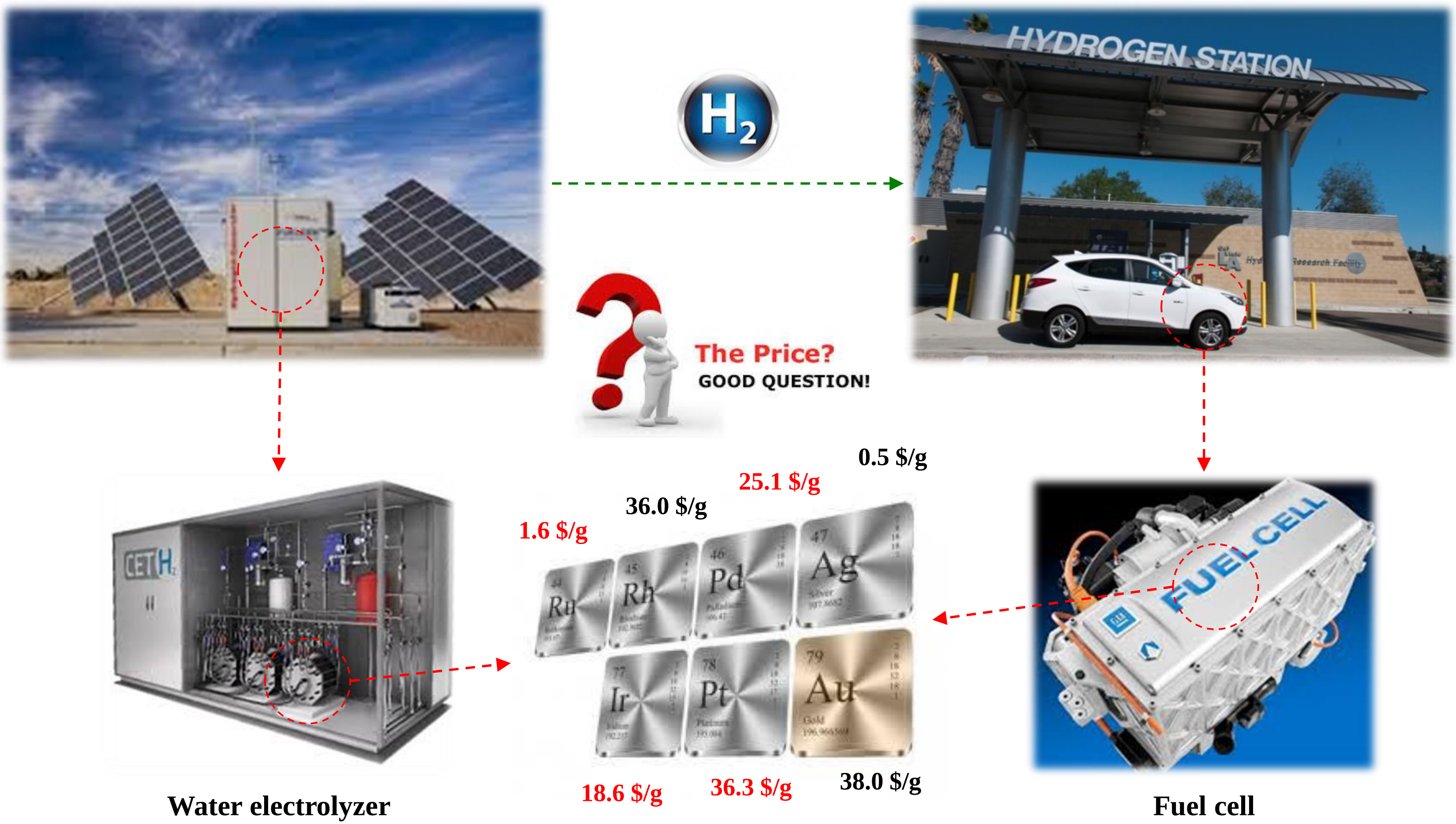


Renewable energy for future

Storage concept

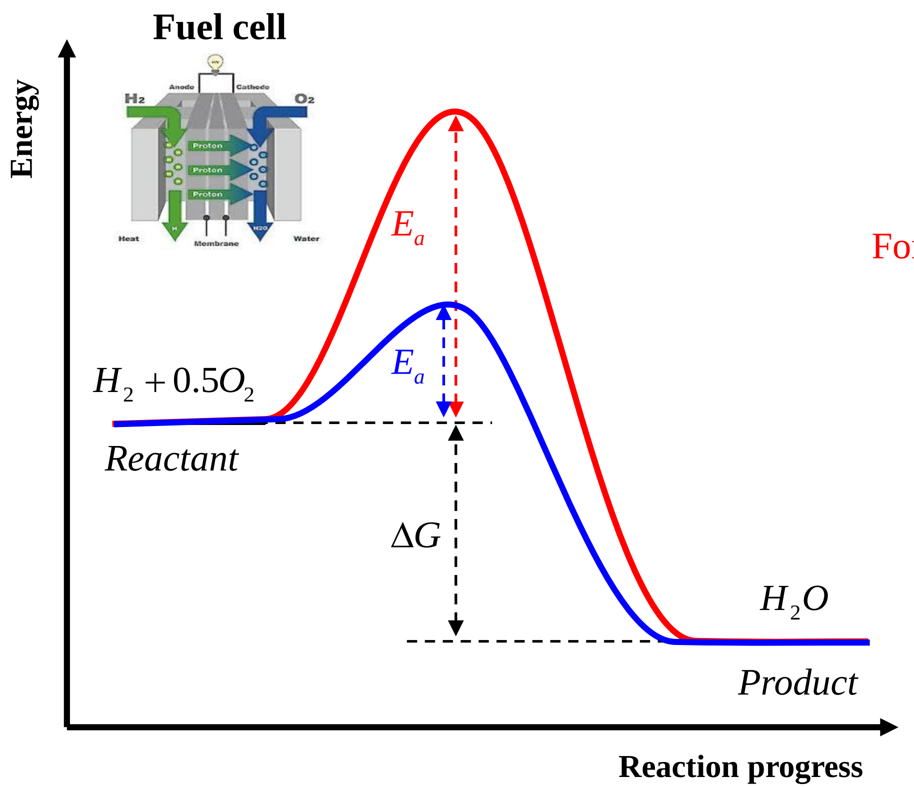


Renewable energy for future



Renewable energy for future

Cost problem (kinetic)



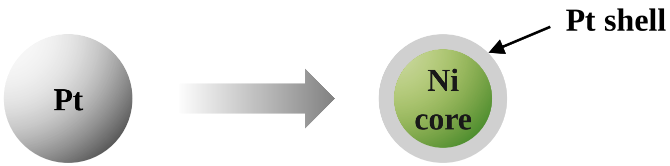
$$H_2 + 0.5O_2 \xrightarrow{r} H_2O$$

$$r = kC_{reatant}, \quad k = Ae^{-E_a/RT}$$

For non-catalyzed reaction $\quad$ For catalyzed reaction

$$k = Ae^{-Ea/RT} \quad < \quad k = Ae^{-Ea/RT}$$

Platinum (Pt) catalyst for fuel cell reactions



36.3 $/g $\quad$ **Lower price**