전기화학 촉매소재 설계

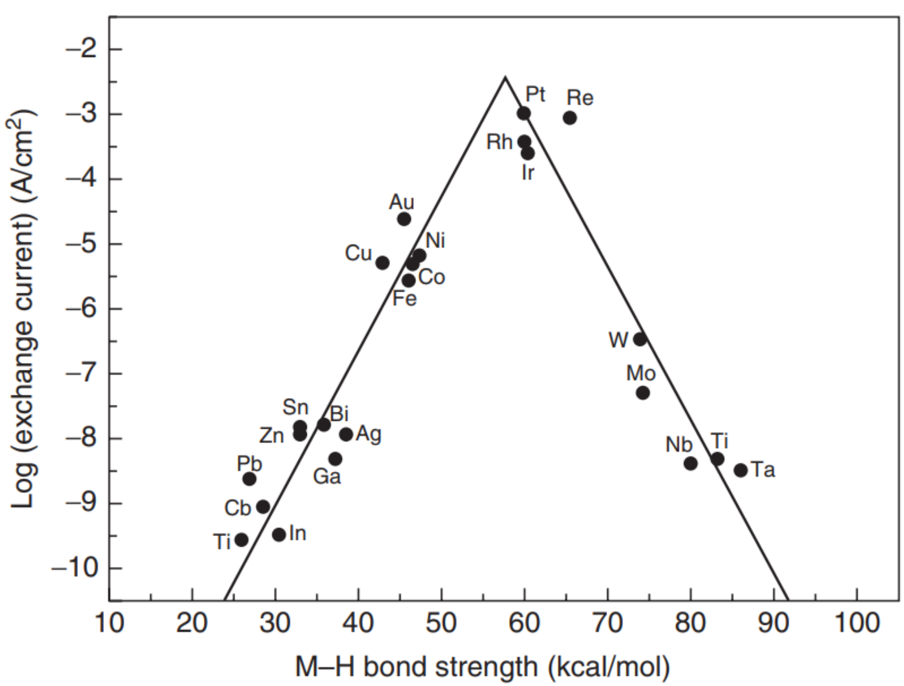
Design of Electrocatalytic Materials

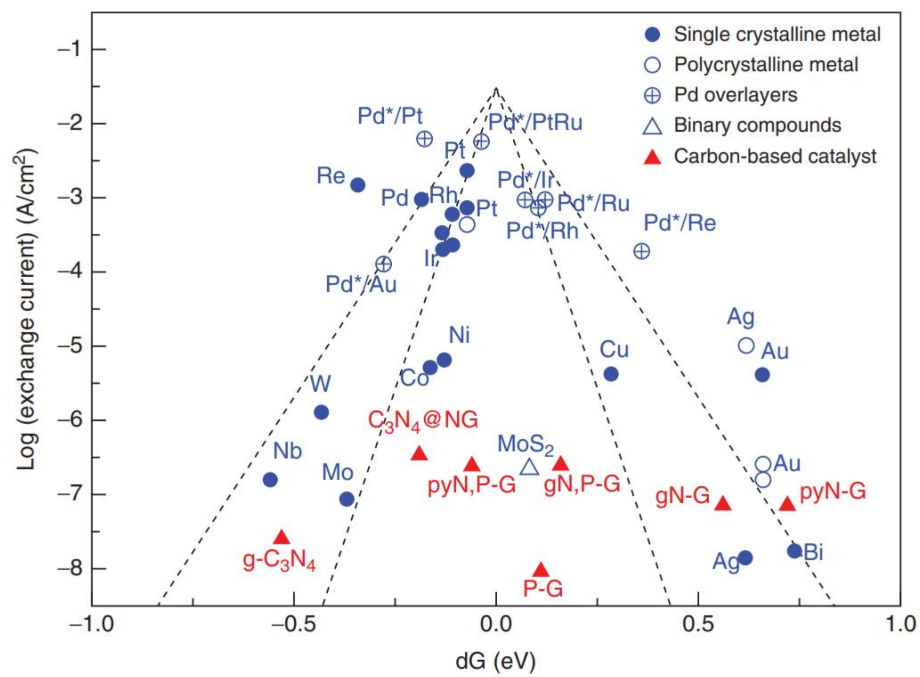
Uk Sim
Department of Materials Science & Engineering
Chonnam National University

Sabatier Principle

Interactions between the catalyst and the substrate should be "just right"; that is, neither too strong nor too weak.

volcano plots

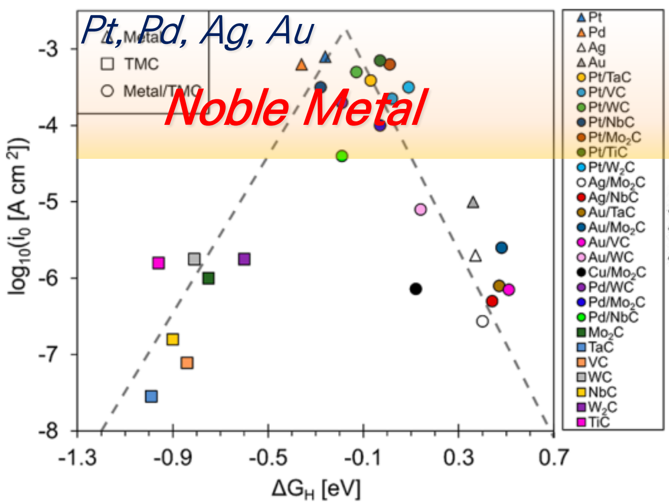




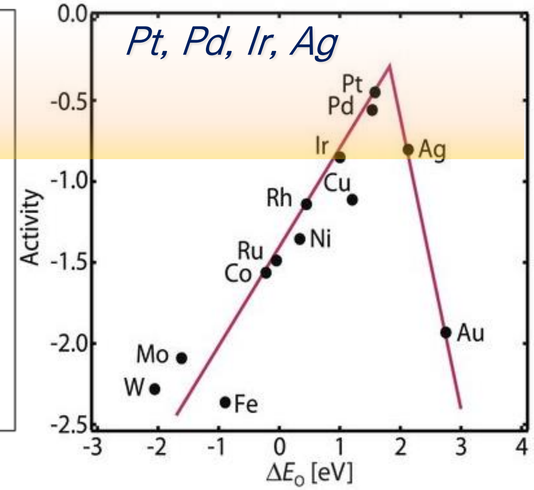
Uk Sim et al., "Hydrogen Production by Electrolysis and Photoelectrochemical System", Handbook of Clean Energy System, John Wiley & Sons, NJ, USA 2015, 5, 1-42

Volcano plots

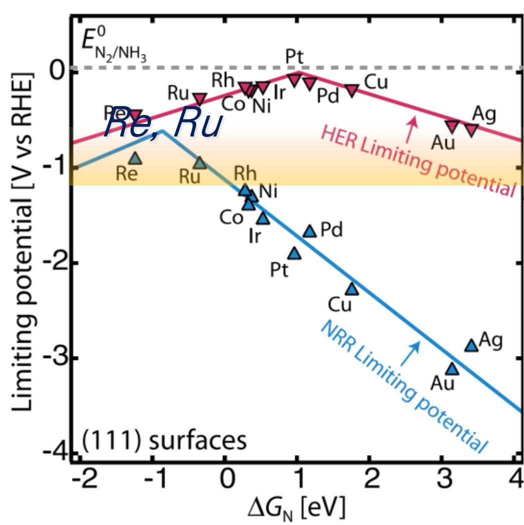
수소발생반응



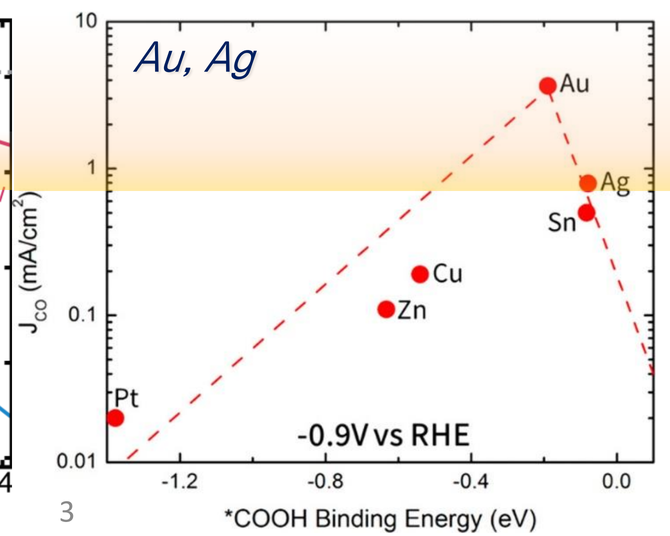
산소환원반응



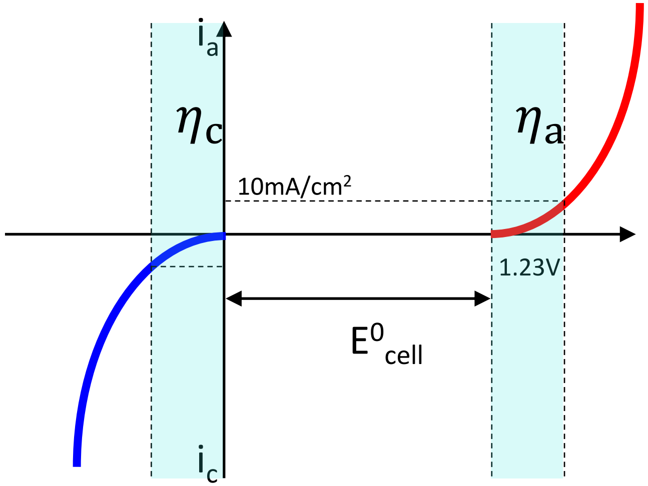
질소환원반응



이산화탄소환원반응



Catalyst for Water Splitting

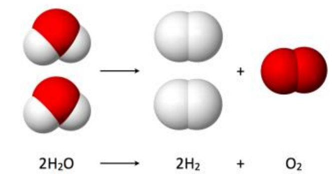


Real voltage required for water splitting

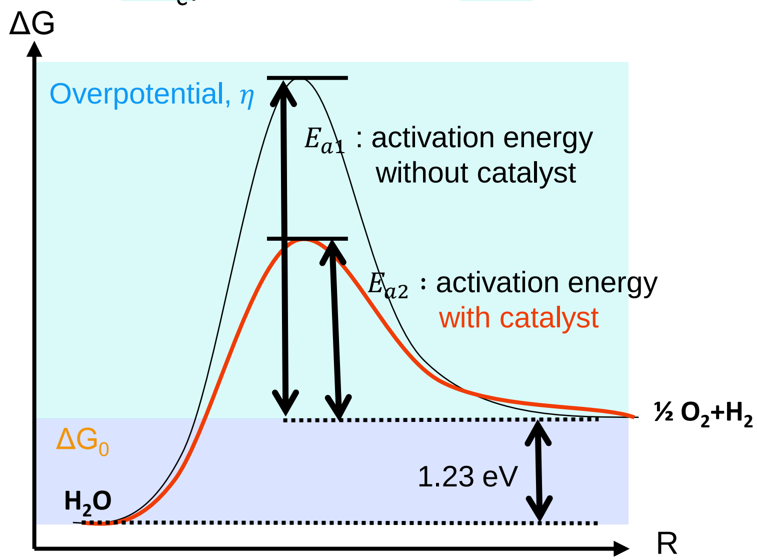
❖ $E_{applied} = 1.23V + \eta_c + \eta_a$

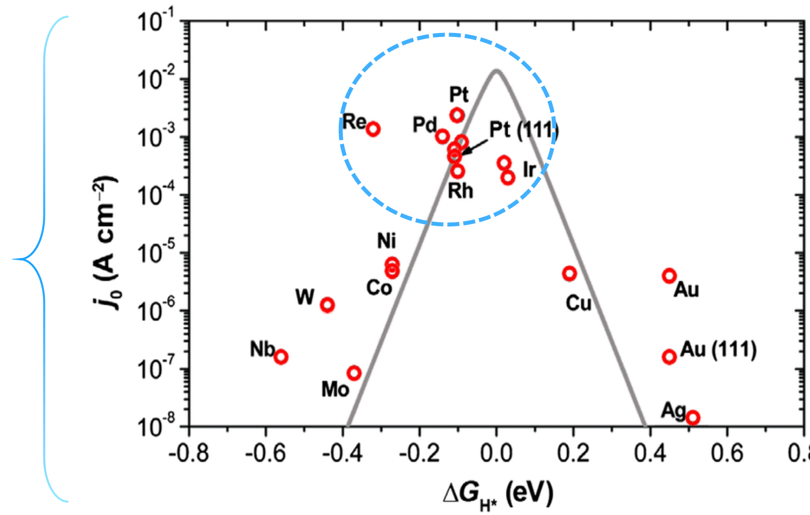
η_c: overpothential at cathode

η_a: overpothential at anode



❖ *As the overvoltage is reduced, E can be reduced, which can be **reduced through the catalyst**.*





Noble materials: high cost, scarcity, and low stability

Electrochemical reactions require **efficient materials** with superior performance for reaching the global outlook of energy conversion.

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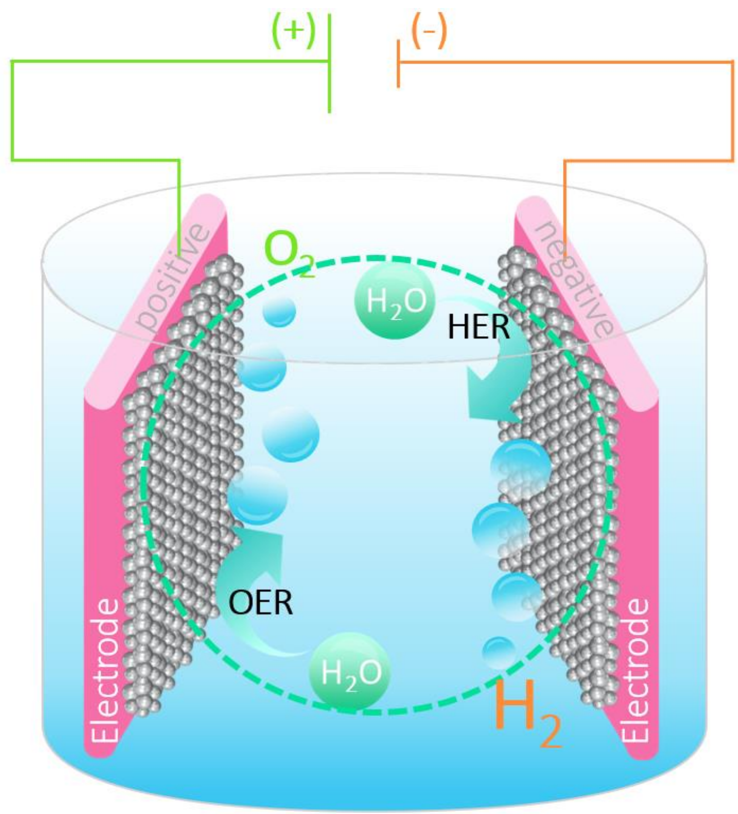
HER, OER mechanism

Full water splitting

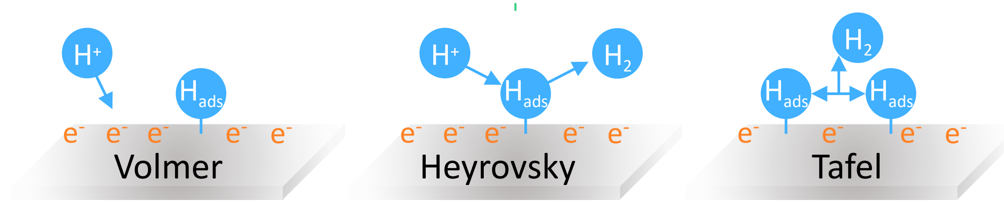


Negative (HER)	Acidic : $2H^+ + 2e^- \rightarrow H_2$ Basic : $* + 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Positive (OER)	Acidic : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Basic : $4OH^- \rightarrow 2H_2O + 4e^- + O_2$

Overall reaction $2H_2O \rightarrow 2H_2 + O_2$

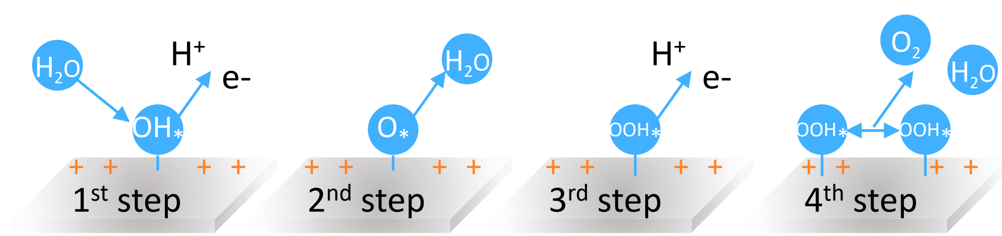
Hydrogen evolution reaction mechanism

acidic condition		basic condition	
Volmer : $* + H^+ + e^-$	$\rightarrow H_{abs}$	$* + H_2O + e^-$	$\rightarrow H_{abs} + OH^-$
Hyerovsky : $H_{abs} + H^+ + e^-$	$\rightarrow H_2$	$H_{abs} + H_2O + e^-$	$\rightarrow H_2 + OH^-$
Tafel : $H_{abs} + H_{abs}$	$\rightarrow H_2$	$H_{abs} + H_{abs}$	$\rightarrow H_2$



Oxygen evolution reaction mechanism

acidic condition	basic condition
1st step : $* + H_2O \rightarrow OH_{ads} + H^+ + e^-$	$* + OH^- \rightarrow OH_{abs} + H^+$
2nd step : $2OH_{abs} \rightarrow O_{abs} + H_2O$	$OH_{abs} \rightarrow O_{abs} + H^+$
3rd step : $O_{abs} + H_2O \rightarrow OOH_{abs} + H^+ + e^-$	$O_{abs} + H_2O \rightarrow OOH_{abs} + H^+$
4th step : $2OOH_{abs} \rightarrow O_{abs} + H_2O + O_2$	$OOH_{abs} \rightarrow O_2 + H^+$



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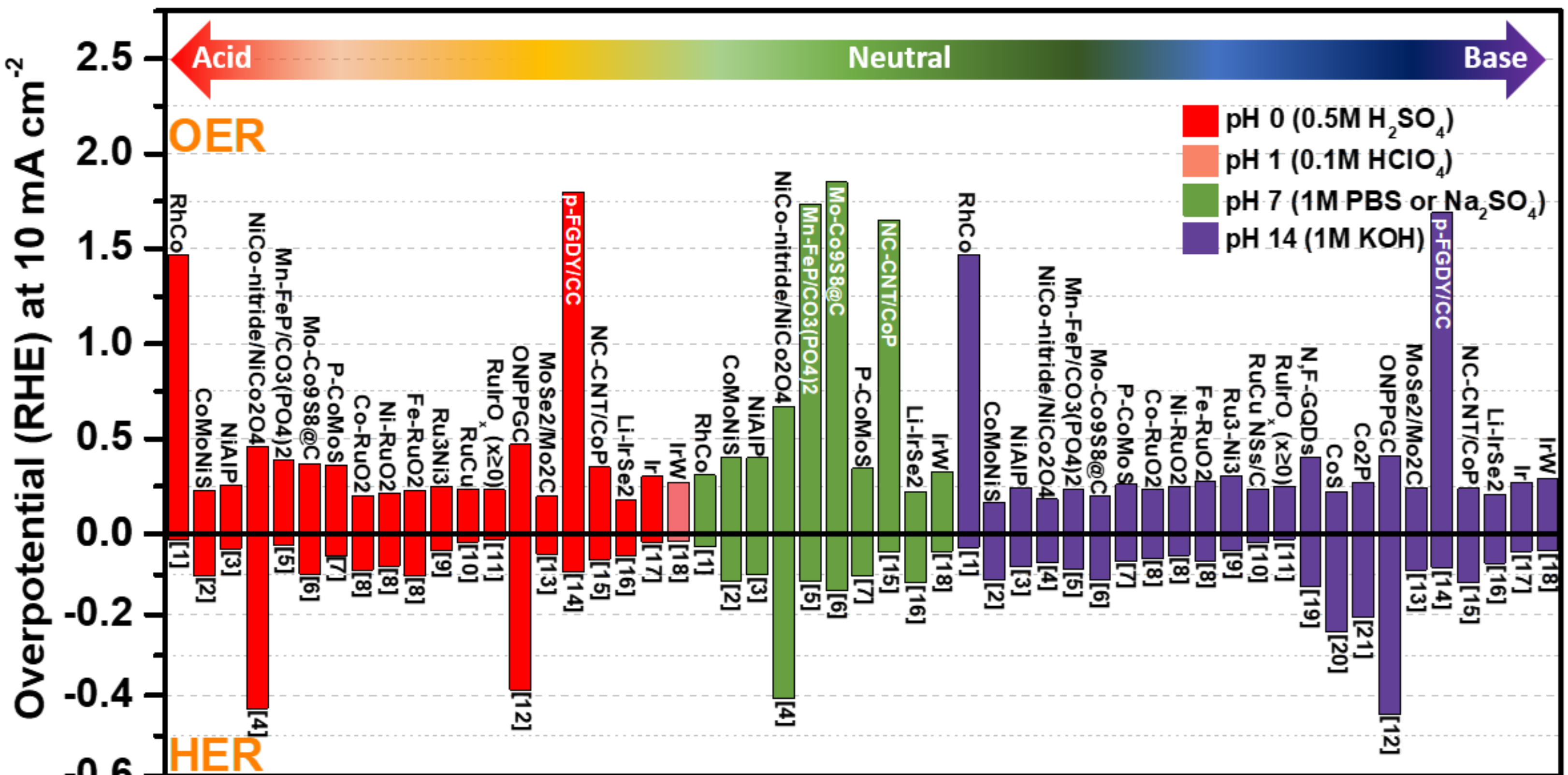
Rational Design of Efficient Electrocatalyst for Full Water Splitting across all pH conditions

Performance of Various Electrocatalysts for Water Splitting over a Wide pH range



G. Janani, Uk Sim et al., MRS Bulletin 2020, 45:7, 539-547*

Nitrogen and Fluorine co-doping in Graphene Quantum Dot for Water Splitting

2D → *Quantum confinement, edge effect* → 0D

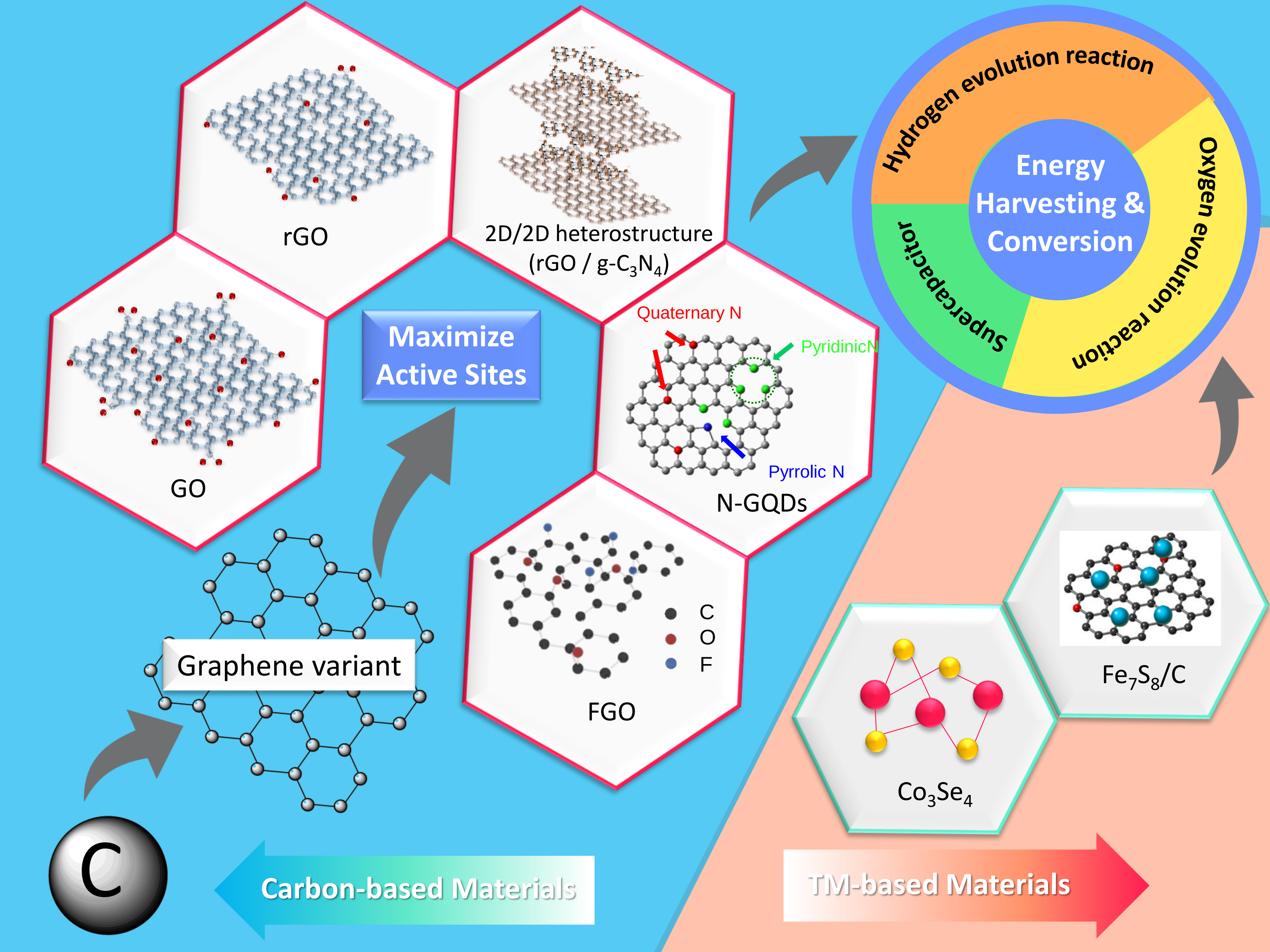
Lateral sizes being reduced to typically < 20nm

intralayer - - - - → *Strong covalent*

interlayer - - - - → *Weak van der Waals*

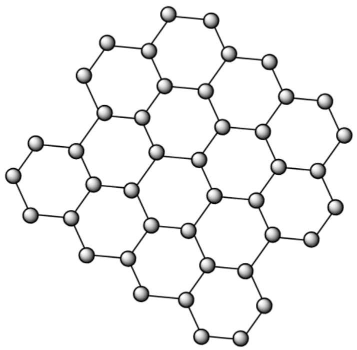
◆ Advantage of 0D materials **(quantum dots)**

- *Edge abundant features*
- *Larger surface-to-volume ratio*
- *Better solubility in both aqueous and nonaqueous solvent*
- *Higher tunability in both aqueous and nonaqueous solvents*
- *Higher tunability in physiochemical properties*
- *Better amenability to hybridize with other nanomaterials*
- *Ease to be doped and functionalized*


rGO
2D/2D heterostructure
(rGO / g-C_3N_4)
GO
Maximize
Active Sites
Quaternary N
PyridinicN
Pyrrolic N
N-GQDs
C
O
F
FGO
Graphene variant
C
Carbon-based Materials
Hydrogen evolution reaction
Oxygen evolution reaction
Supercapacitor
Energy
Harvesting &
Conversion
Fe_7S_8/C
Co_3Se_4
TM-based Materials

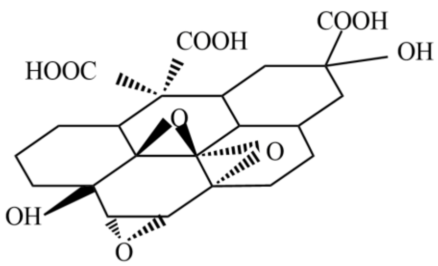
reduced Graphene Oxide Deposited on Silicon Nanowire for HER

◆ Graphene



- *High thermal conductivity (~5000Wm-1K^{-1})*
- *Superior carriers mobility (200,000 cm2V^{-1}s^{-1})*
- *High transparency (~97.7%)*
- *High theoretical specific surface area (~2630m2g^{-1})*
- *Zero band gap*

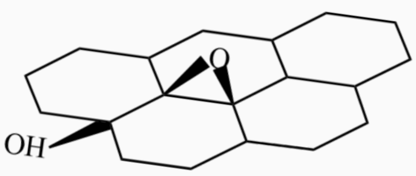
◆ Graphene oxide (GO)



- *Low material cost*
- *Electrically insulating*
- *Reliable and exceptional synthesis process*
- *Weak van der Waals interaction*
- *Synthesis by Hummer's method*

reduction

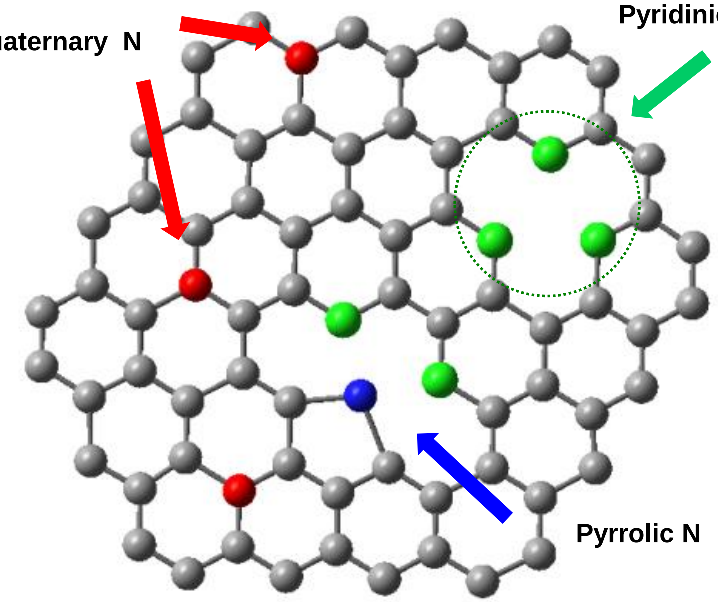
◆ Reduced Graphene oxide (rGO)



- *High electrical conductivity (resulted from better graphitization of C=C π-conjugation of the graphene basal plane)*
- *Large specific surface area*
- *High electron mobility*
- *Reduced by hydrazine hydrate*

Nitrogen doping in Graphene Quantum Sheets

Nitrogen doping effects



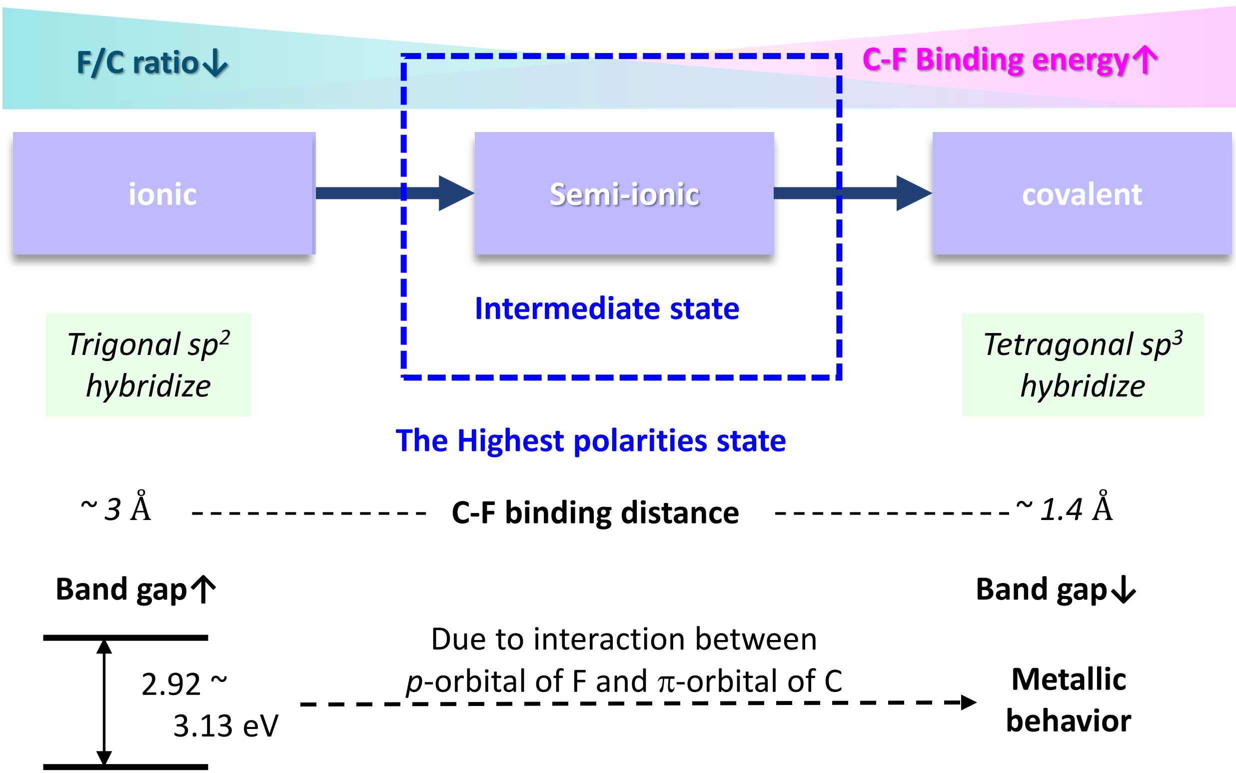
- *GQD with chemically bonded N atoms could alter their electronic characteristics and offer more active sites*
- *carbon adjacent to an N atom can cause a positive shift in Fermi energy, which was a benefit for the charge transfer*

- *Pyridinic : N atoms at the edge of six-membered ring*
- *Pyrrolic : N atoms at the edge of five-membered ring*
- *Graphitic : the substitutional site in graphene plane*
- *As the nitrogen doping time increases, the order of pyridinic, pyrrolic and others dominant.*
- *The doping to pyridinic and pyrrolic sites increases the work function*

Uk Sim et al., Energy Environmental Science 2015

Nitrogen and Fluorine co-doping in Graphene Quantum Dot for Water Splitting

Fluorine doping effects



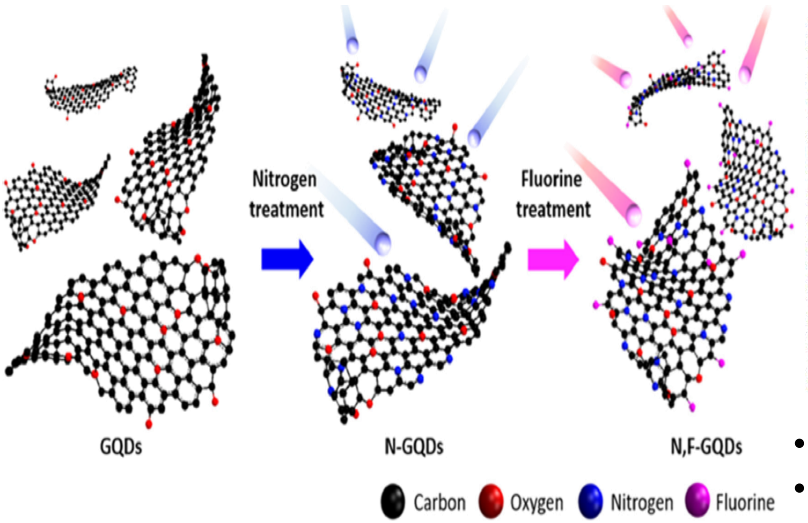
- *fluorine functionalization could alter the electronic state*
- *the bonding interaction between C and F can change ionic, semi-ionic, and covalent configurations owing to the strong electronegativity of fluorine*
- *With increasing F/C ratio, the C-F bonds change their character from ionic to semi-ionic to covalent one.*
- *the semi-ionic C-F bonding doped with ~4% fluorine could enhance the electrical properties of the electrode and facilitate electron transport through the active material*

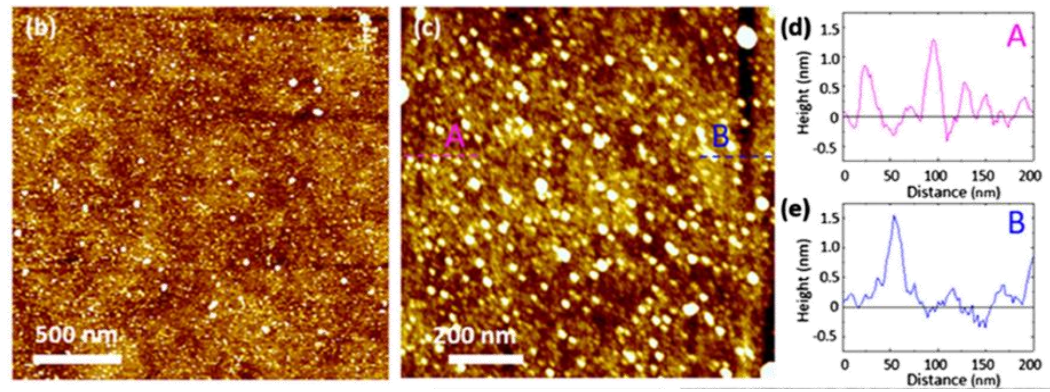
Uk Sim et al., Chemical Engineering Journal 2022 accepted*

N,F-GQDs for water splitting

Uk Sim et al., Applied Surface Science 507 (2020) 145157*

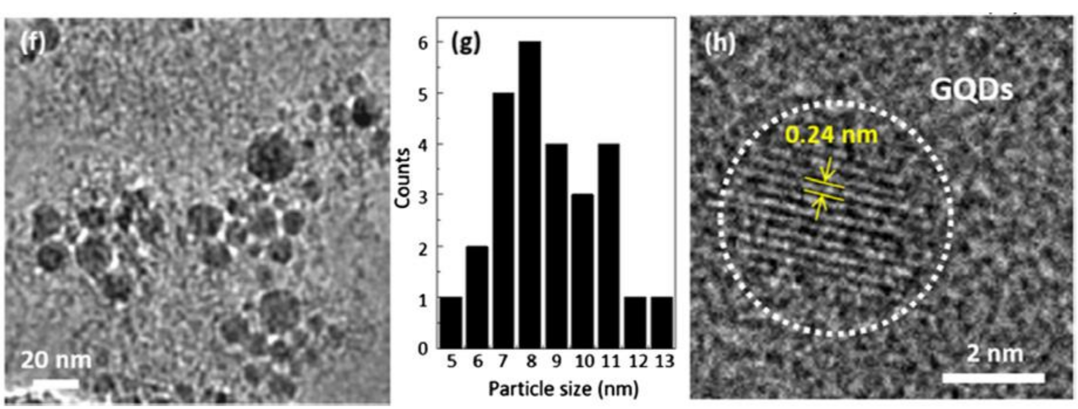
➢ AFM images of the GQDs dispersed of a SiO_2 substrate and height profiles





- Homogeneous N,F-GQDs particles were uniformly placed on the Si.
- An average under 1.5 nm height of N,F-GQDs, which indicates the number of layers in N,F-GQDs was about ~ 3 layers.

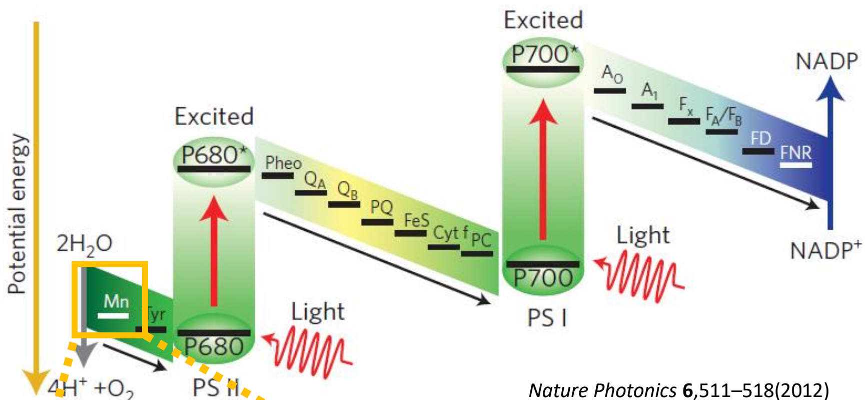
➢ TEM images and histogram showing the size distribution of GQDs



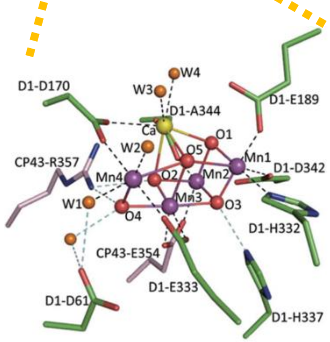
- Most of N,F-GQDs dispersed on graphene sheet show a size distribution from 2 to 10 nm with an average size of 8.7 nm.
- The lattice structure shown in the high-resolution TEM image indicates the N,F-GQDs are highly crystalline.

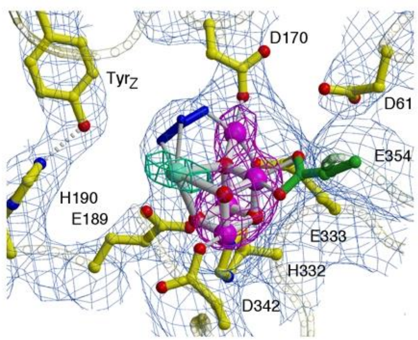
Natural enzyme

Oxygen Evolution



Nature Photonics **6**,511–518(2012)





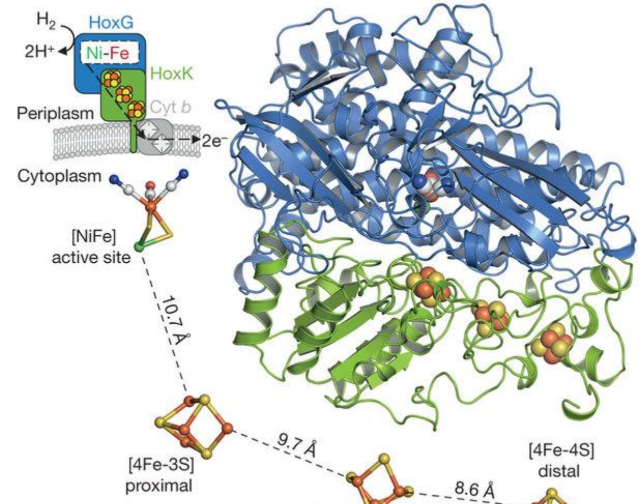
Nature **473**, 55–60 (2011)

Science **303**, 1831-1838 (2004)

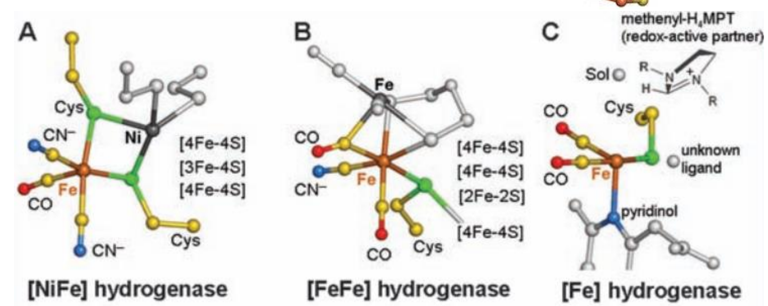
$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

PSII and Mn_4CaO_5 cluster

Hydrogen Evolution



Nature **479**, 249-252 (2011)



Science **321**, 572-575 (2008)

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

Hydrogenase and [Fe–S] cluster

C.japonica derived Sulfur-doped Activated Carbon

Biomass

Earch abundant

Low cost and renenue source

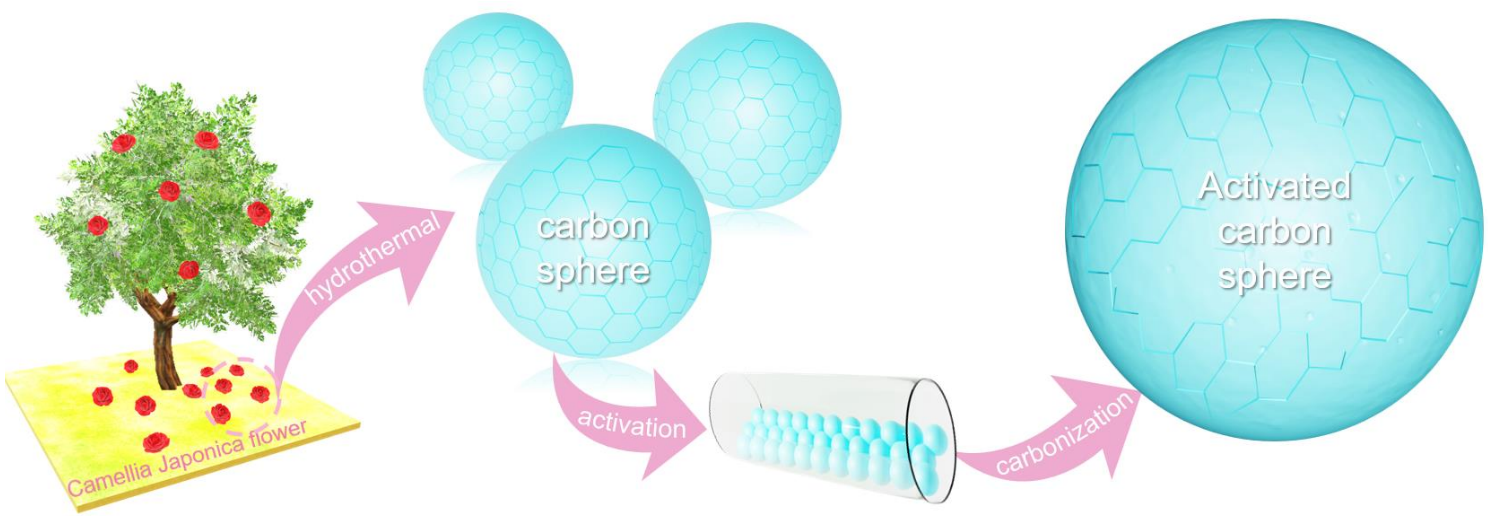
Industrial production

Thermal treatment

Gas production

CO_2 emission

Camellia japonica flower was applied to catalysts for operating electrochemical reactions without emission of CO_2.



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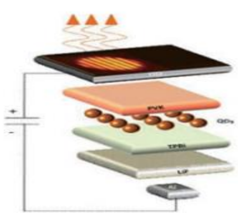
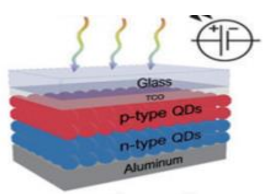
Metal anchored carbon quantum dots

Carbon quantum dots

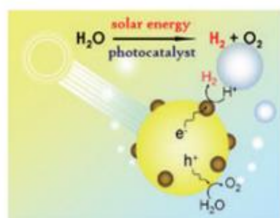
- Non-toxic
- Environmentally friendly
- High photostability
- High chemical stability
- Easy surface functionalization
- High electric conductivity



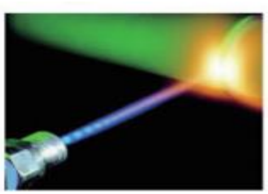
QD LED



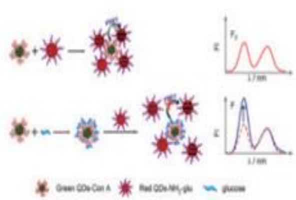
Solar cell



catalysts

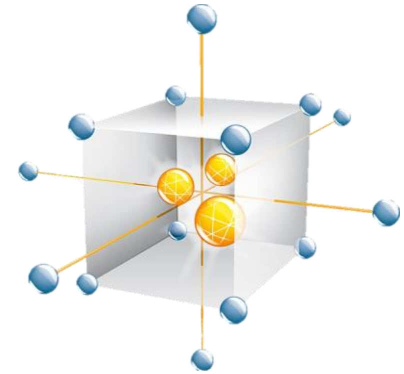


lasing



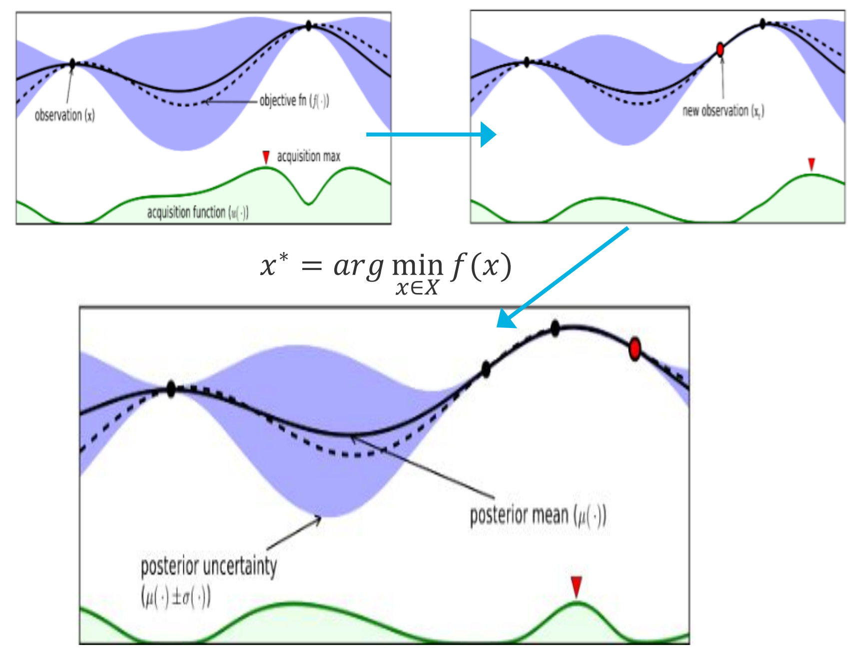
Bio sensor

Design of experiments (DoE)



the design of experiments (DoE) is considered to discover superior performance of the prepared catalysts.

Machine learning: optimization method – Bayesian algorism



$$x^* = arg \min_{x \in X} f(x)$$

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