광전기화학 시스템 조촉매 소재 설계

Design of Co-catalysts in PEC System

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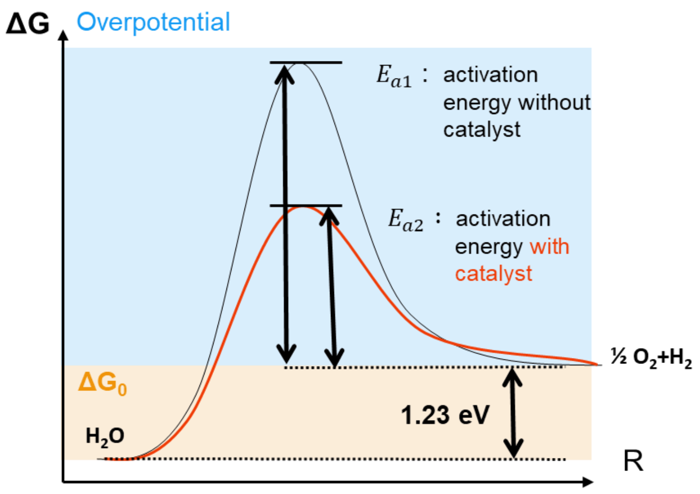
Water Splitting and Catalysts



Cathode
Hydrogen Evolution Reaction (HER)

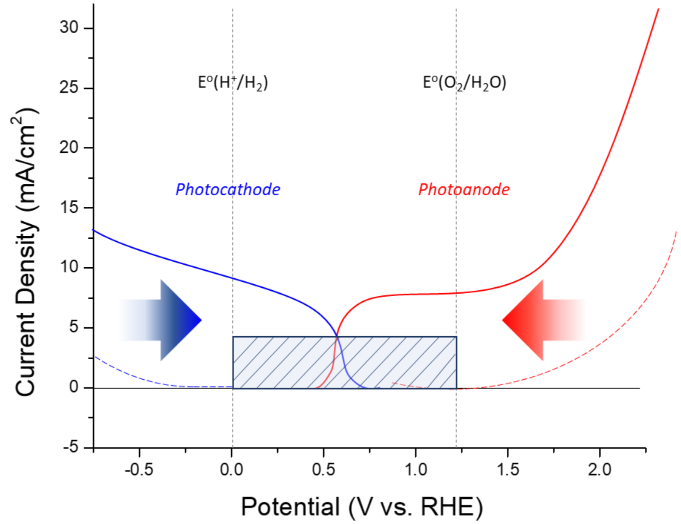
$$4H^+ + 4e^- \leftrightarrow 2H_2 \quad E^0{}_{red} = \pm 0.000\ V - 0.059\ [pH]\ vs.\ NHE$$

Anode
Oxygen Evolution Reaction (OER)

$$2H_2O + 4h^+ \leftrightarrow 4H^+ + O_2 \quad E^0{}_{ox} = 1.229\ V - 0.059\ [pH]\ vs.\ NHE$$

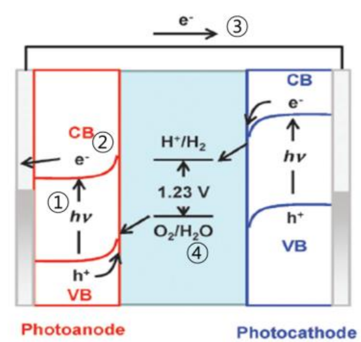
$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \quad E^0 = 1.229\ V$$

- In water electrolysis, catalysts reduced the overpotential that is required for the water splitting reactions
- Photoelectrochemical system utilizes photon energy to compensate the overpotential



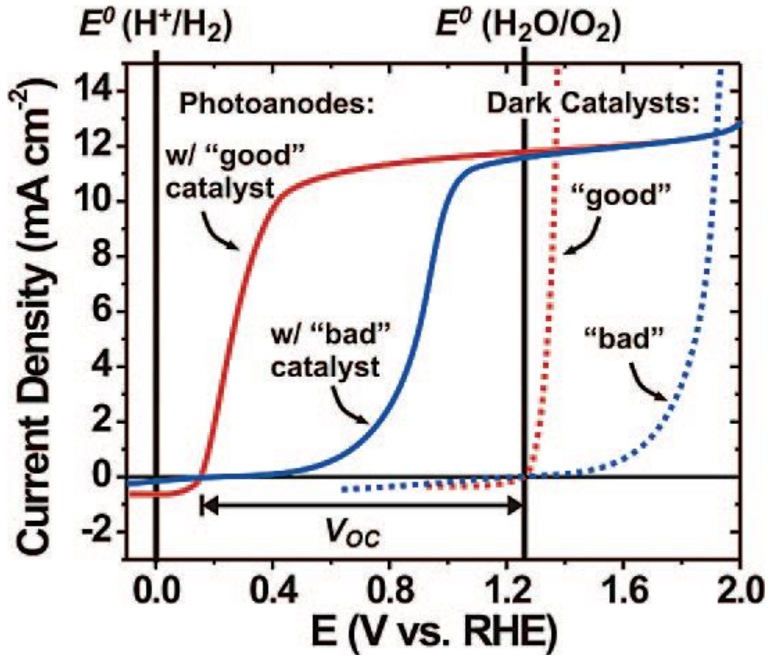
Increase of current in between 0 – 1.23 V potential region

① Absorption of Light
② Charge Generation
③ Carrier Separation
④ Redox Reaction



Effect of Surface Catalyst

Qualitative effect of surface catalysts on photoanode performance



Catalyst

1. Improvement of photoelectrode kinetics
2. Change of energetics of the electron transfer process

Good Catalyst

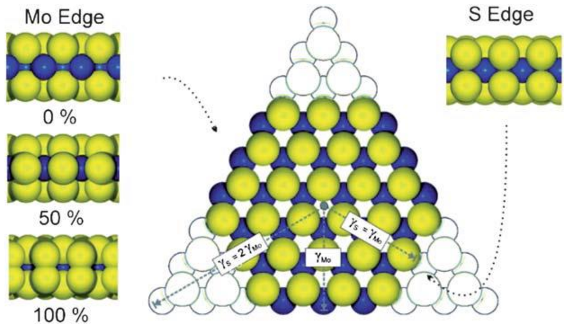
1. Highly active (producing large quantities of H_2 or O_2 quickly)
2. Robust enough to maintain its efficiency over time scales

Michael G. Walter et al., Chem. Rev, 110, 6446, (2010)

Catalyst Materials for Hydrogen Evolution

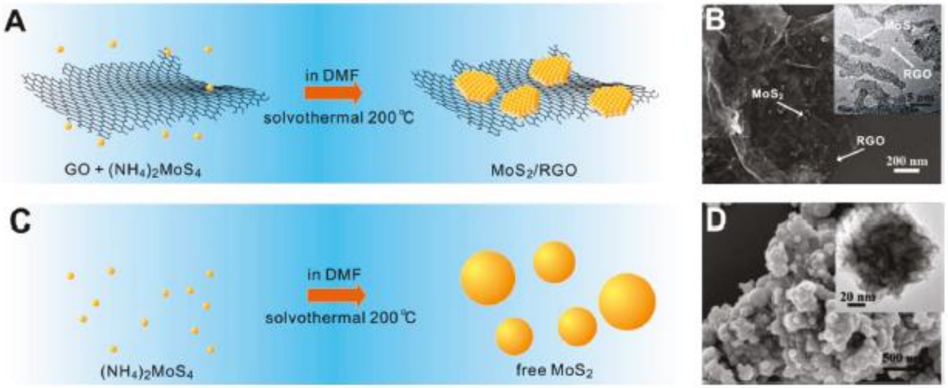
Pure Metals	Metal composites/ alloys	Compounds that incorporate nonmetallic elements	Molecular catalyst
Pt, Pd, Ni, Co, Fe, Mo, …	**Ni-Mo, Ni-Co, Ni-Mo-Cd, Ni-Mo-Fe, …**	**Metal Oxide (RuO_2, Sr_xNbO_{3-d}), Sulfides, Tungsten Carbides, Silicotungstates**	**Nickel and Cobalt Macrocycles Nickel and Cobalt Macrocycles…**

Bio-inspired MoS Catalysts for hydrogen evolution



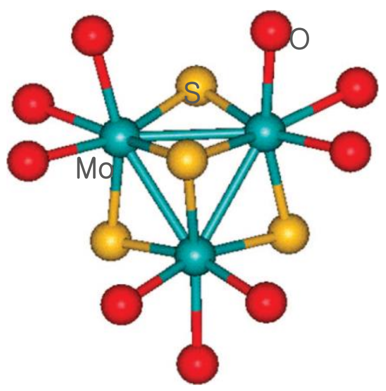
MoS_2 nanocrystal

Phys. Rev. Lett., 2000, **84**, 951
J. Catal., 2004, **221**, 510



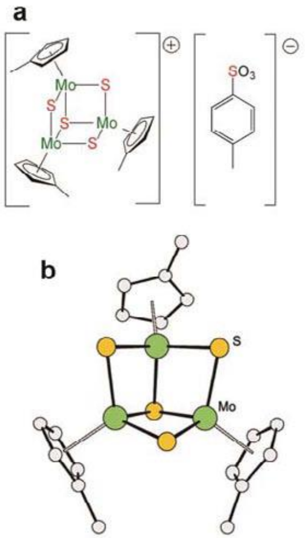
MoS_2 nanoparticles on Graphene

JACS Comm., 2011, **133**, 7294



Incomplete Cubane-type $[Mo_3S_4]^{4+}$

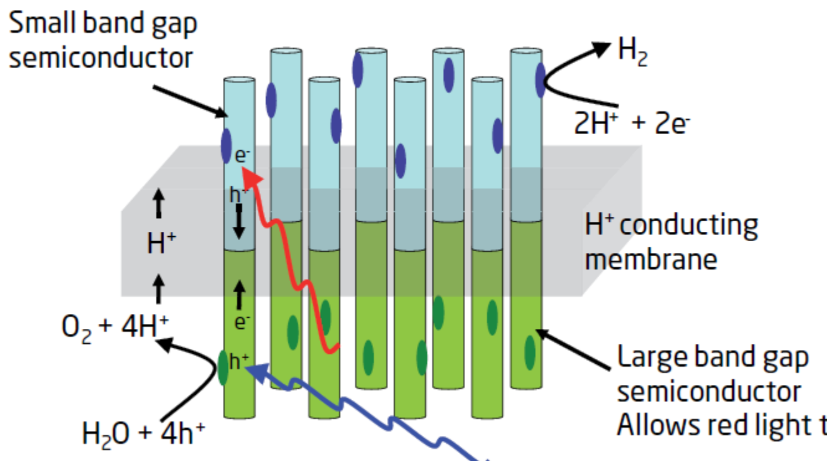
J. Phys. Chem. C, 2008, **112**, 17492

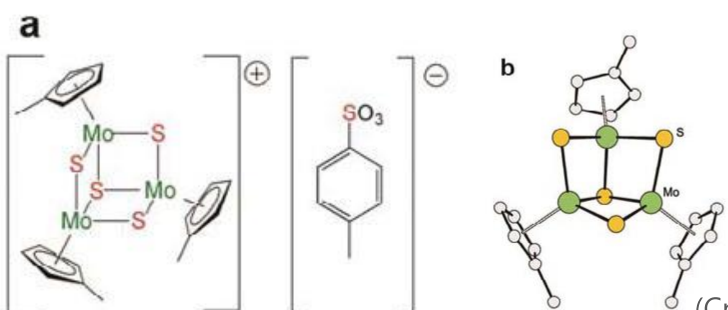


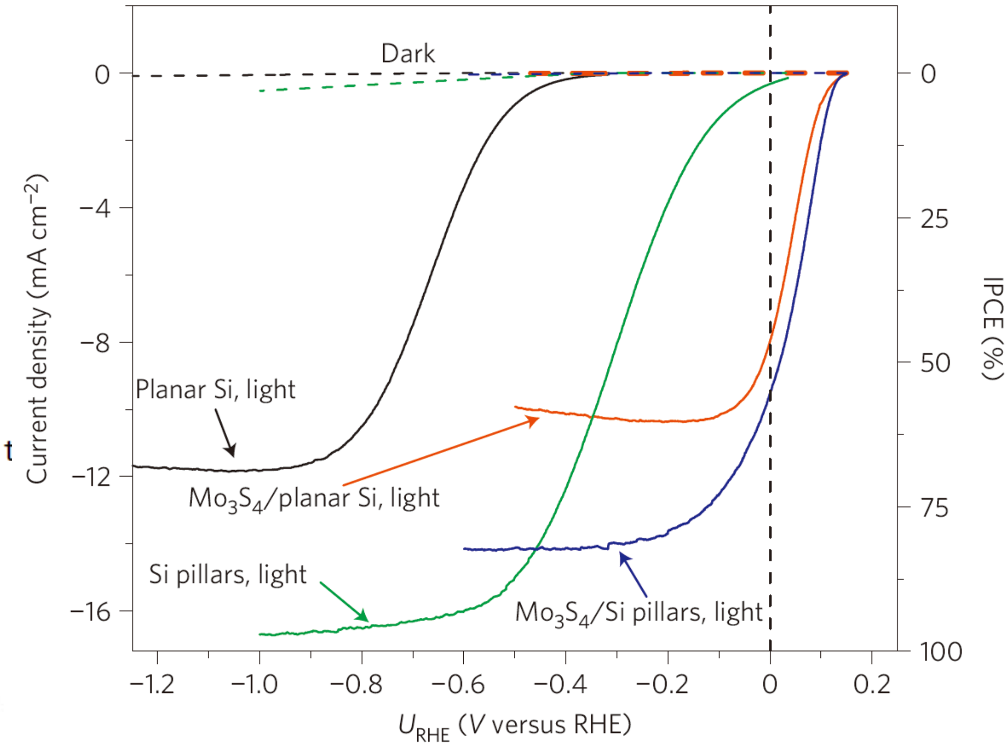
Mo_3S_4 molecular co-catalyst

Nat. Mater., 2011, **10**, 434

Mo_3S_4 co-catalysts bonded to a silicon photocathode for solar hydrogen evolution







[(η^5-Cp′)$_3$Mo$_3$S$_4$][pts]
(Cp′= methylcyclopentadienyl,
pts = *p*-toluenesulfonate)

Two photon process system: Ideal chemical tandem solar cell

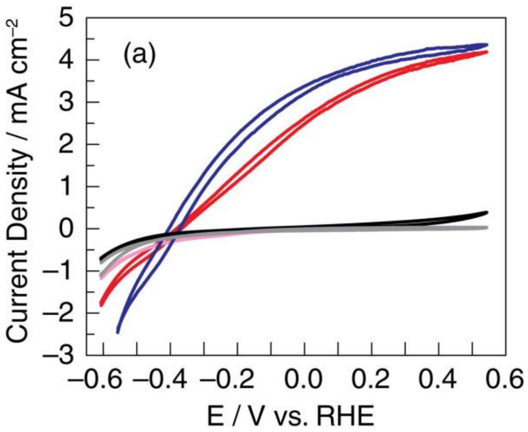
10 % of the energy supplied from the sun at peak intensity = ~8mA/cm^2 at both cathode and anode

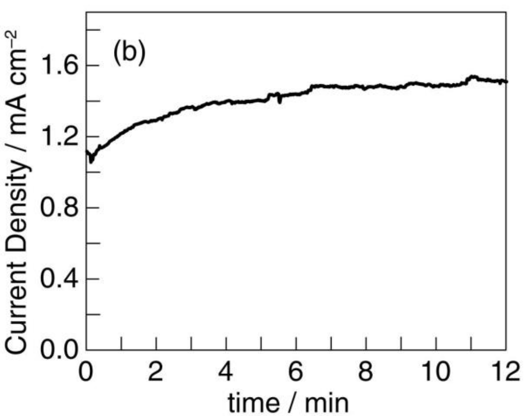
Si(1.12eV bandgap): Excellent for capturing photons in the red part of the solar spectrum

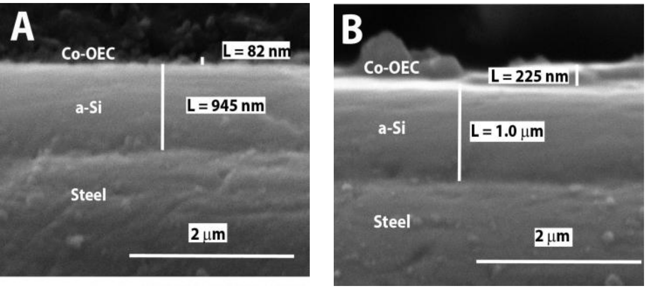
Pillar structure vs. planar structure

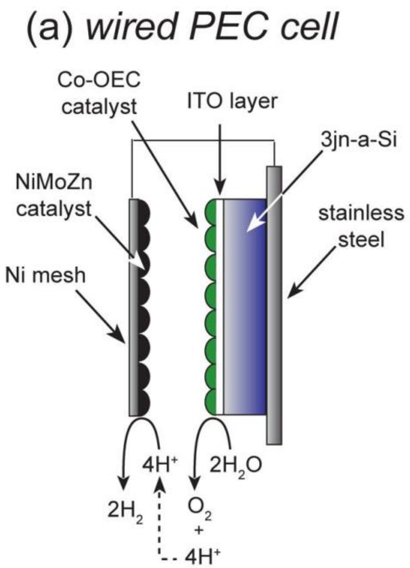
Nat. Mater., 10, **2011**, 434

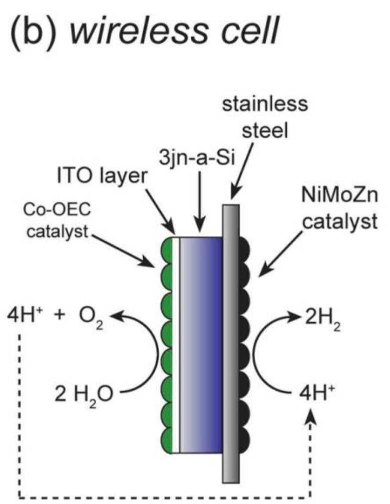
Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts

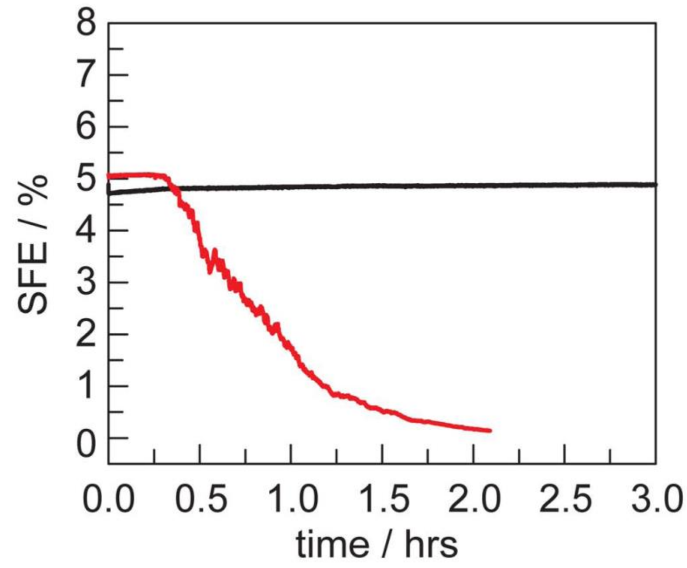


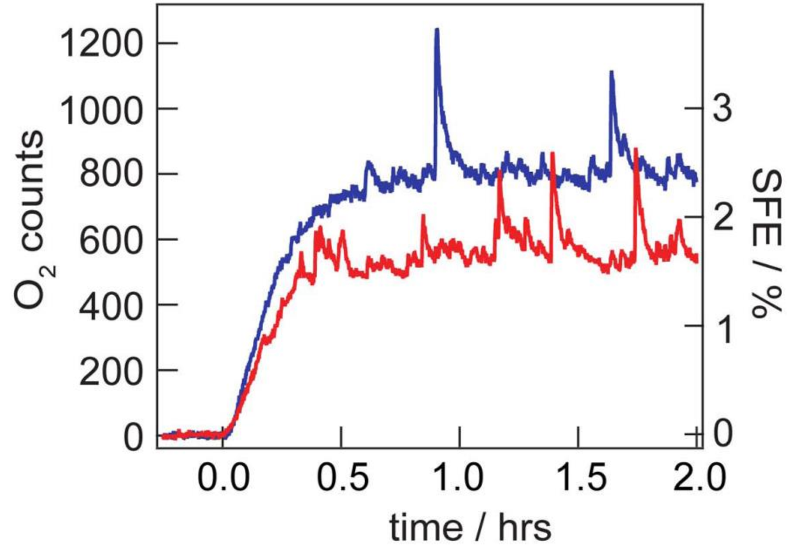






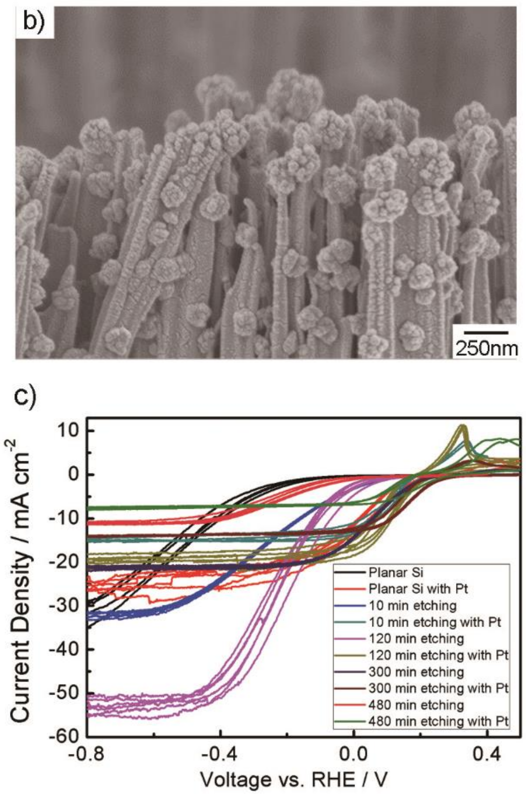


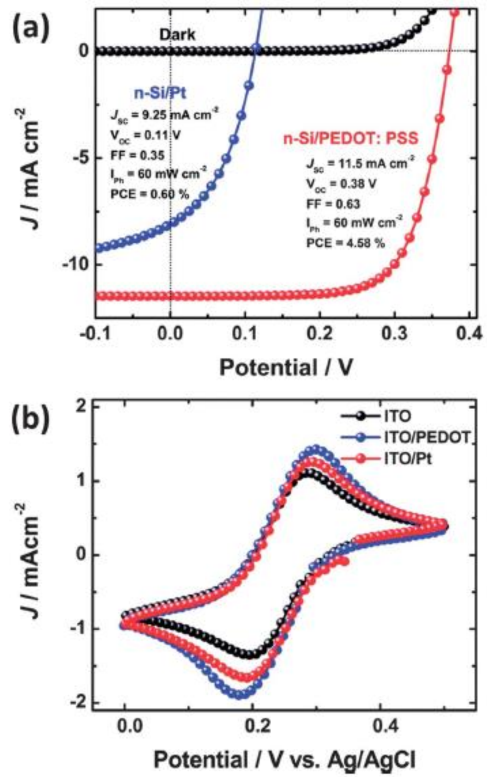


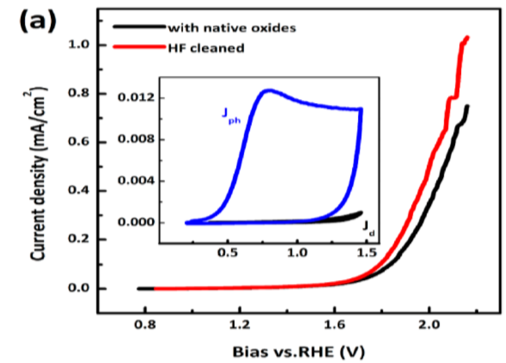


Steven Y. Reece et al., Sciencexpress, 29 september

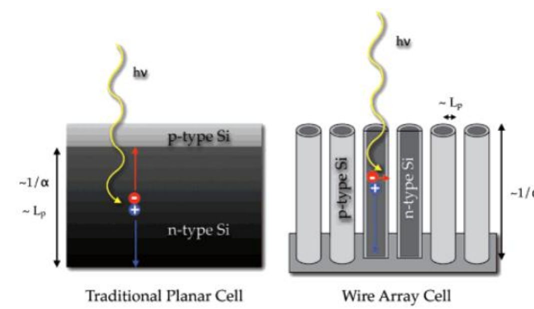
Disadvantages of Previous Catalyst on PEC







Nano Lett., Article ASAP

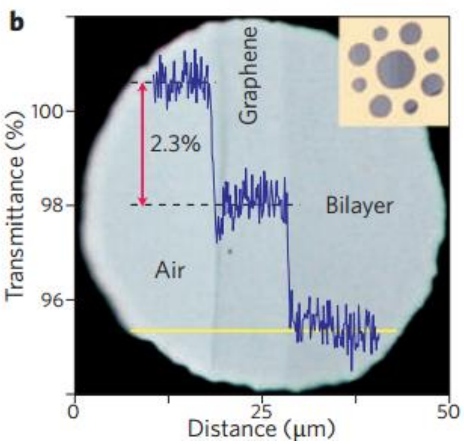


J. Mater. Chem. A, 2013,**1**, 5414-5422 ***Energy Environ. Sci.***, 2013,**6**, 1633-1639 ***J. Phys. Chem. C***, 2008, ***112*** , 6194–6201

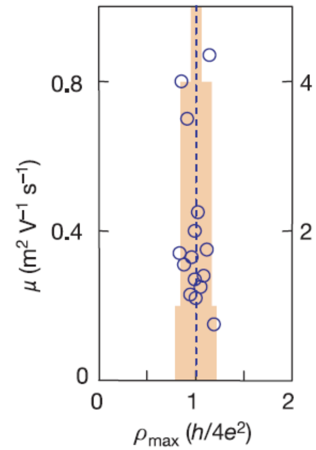
- **In PEC, negative effects from catalysts should be considered:**
  1) reflection by the overlaid catalyst, 2) an unfavorable band structure such as a Schottky barrier, 3) photocorrosion, and 4) recombination sites at the interface.

➢ **To design catalysts for photoelectrochemical water splitting, the optical properties, stability and interfacial issues must be comprehensively considered.**

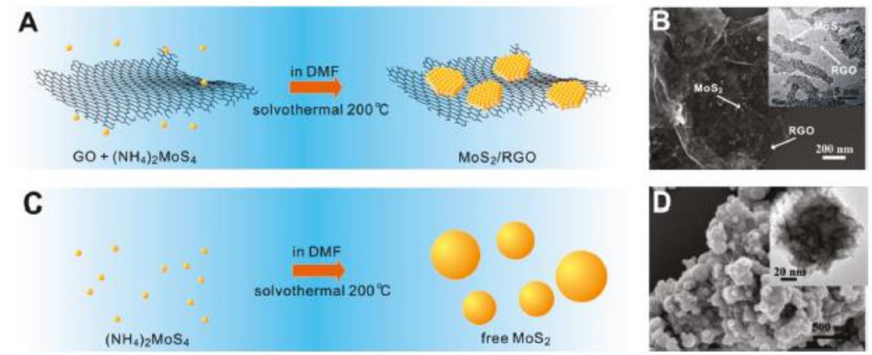
Carbon-based catalysts



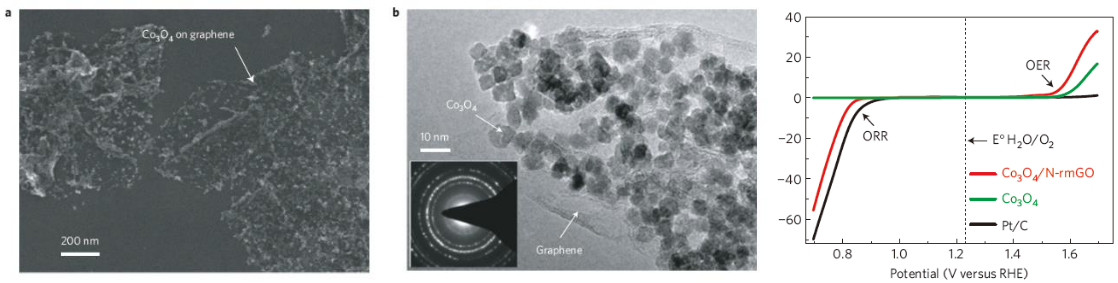
Science, 2008, ***320***, 1308–1308



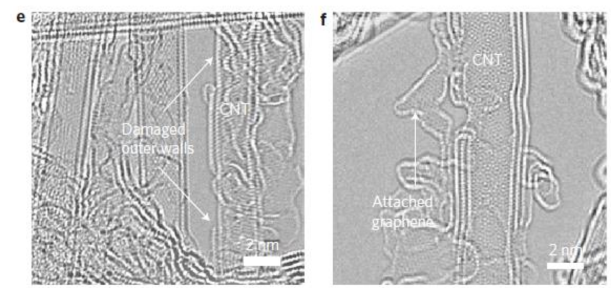
Nature, 2005, ***438***, 197-200



J. Am. Chem. Soc., 2011, ***133***, 7294-7299



Nature Mater. 2011, ***10***, 780-786

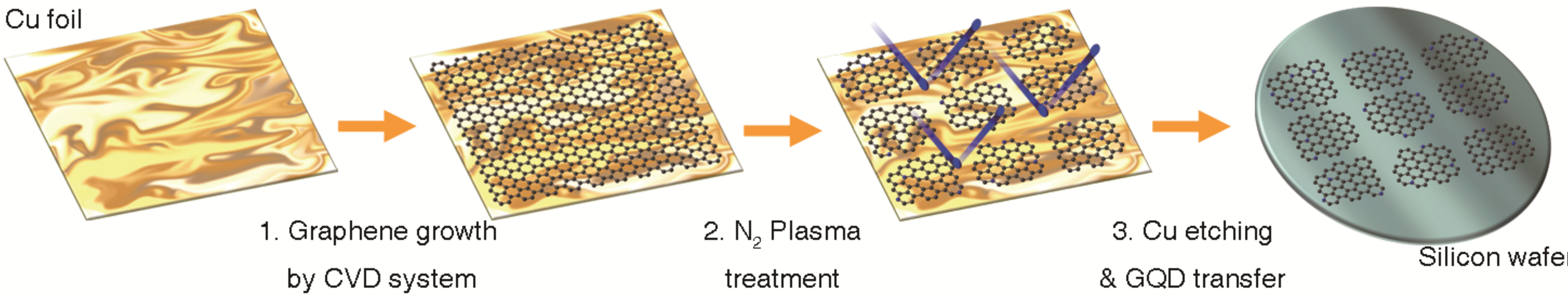


Nature Nanotech. 2012, **7**, 394-400

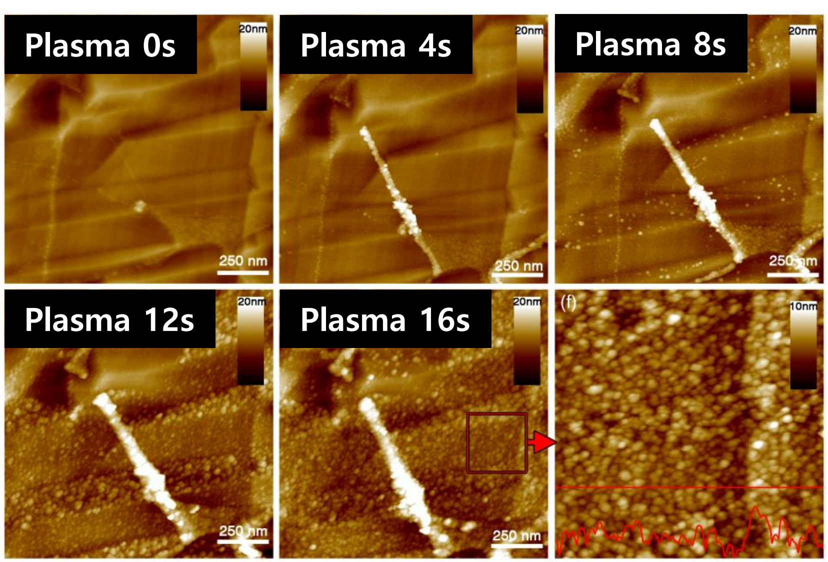
- Carbon-based catalysts: non-precious, environmentally benign, and corrosion resistant catalysts
- Graphene: excellent transmittancy and superior intrinsic carrier mobility
- It has been reported that reduced graphene oxide (rGO) containing catalytic active materials exhibited improved activity in HERs, oxygen evolution reactions (OERs), and oxygen reduction reactions (ORRs)

Preparation of Graphene, NGr/Silicon photocathode

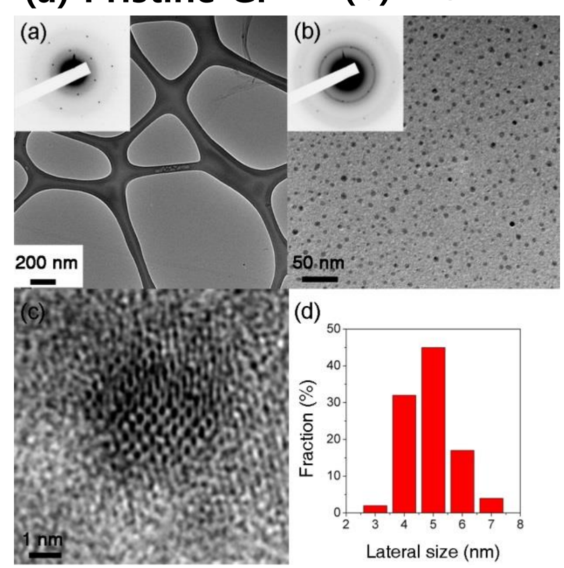
- **Process for Nitrogen doped Graphene Quantum Dot(NGr)**



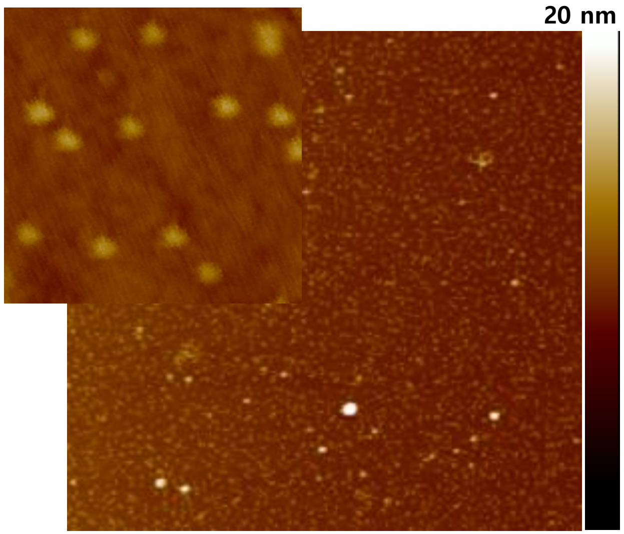
- **Morphology transition of Graphene via plasma treatment**

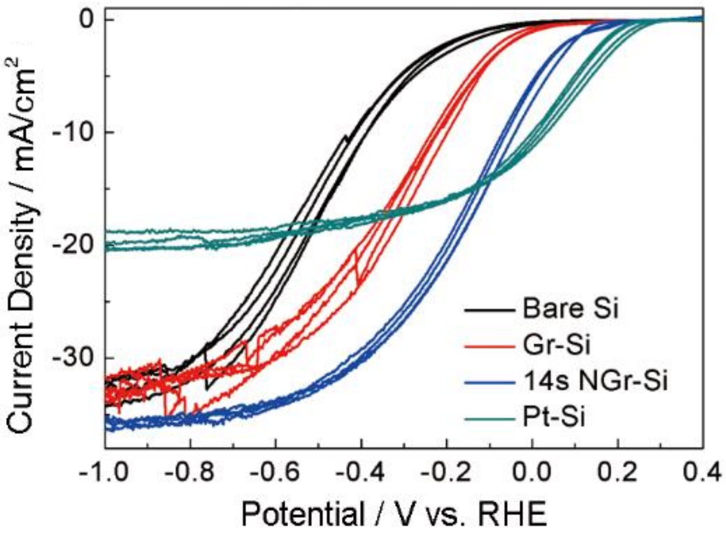


(a) Pristine Gr **(b) NGr**



The effect of Graphene catalyst on Si photocathode





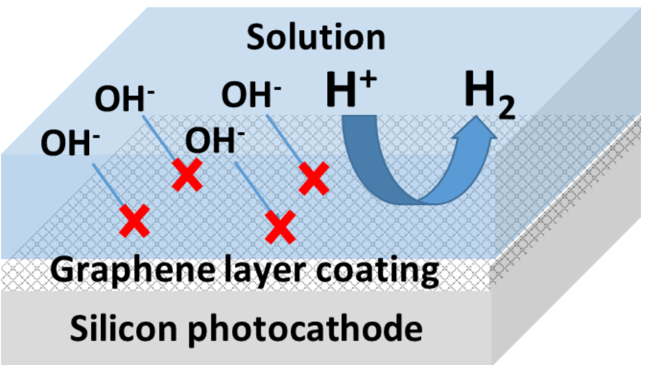
N-doped monolayer graphene catalyst enhanced the PEC performance of a Si-photocathode.

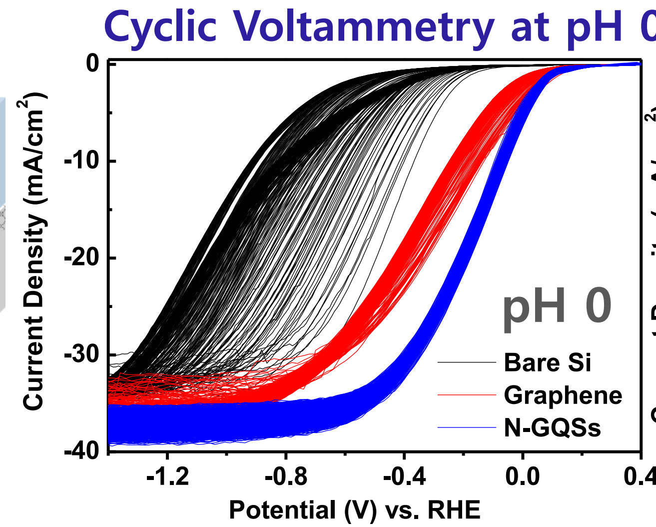
The onset potential for photocurrent from the Si was significantly shifted toward the anodic direction without a change in the saturation current density.

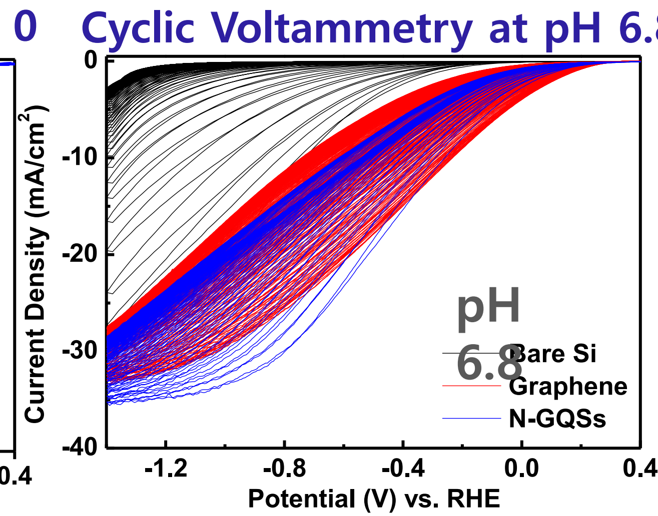
NGr has excellent catalytic activity for photoelectrochemical HER on the Si photocathode

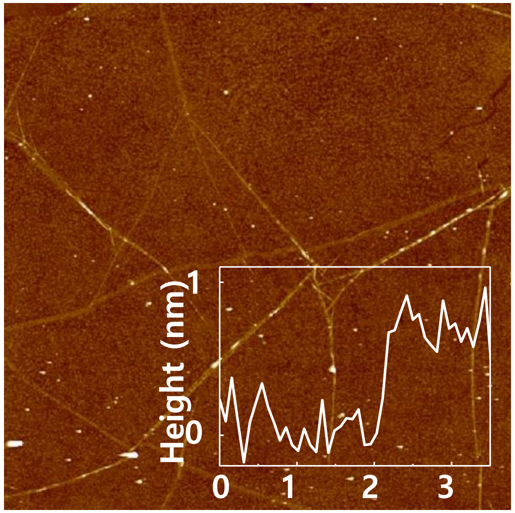
NGr is a passivation layer that maintains a higher onset potential and current density even at neutral pH.

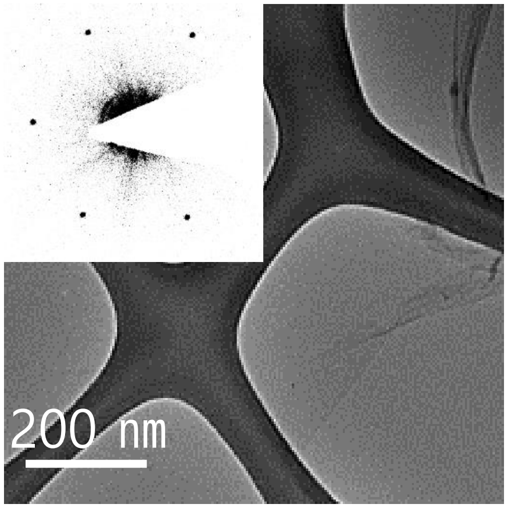
Onset potential (V_{os}) Enhancement

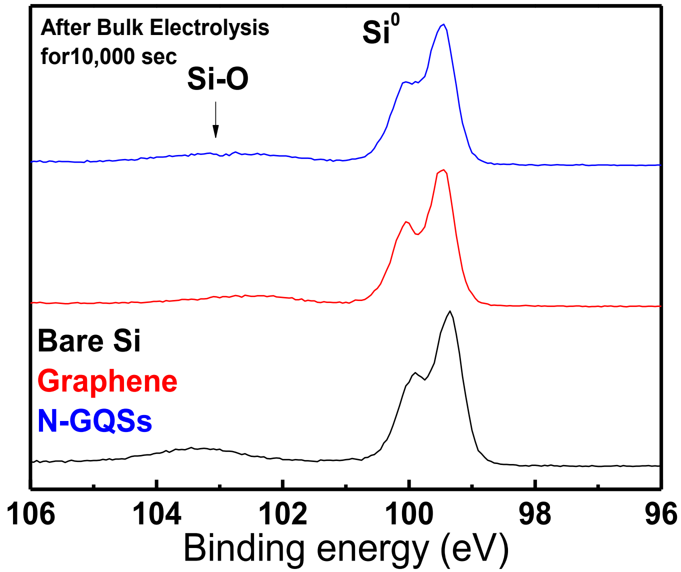










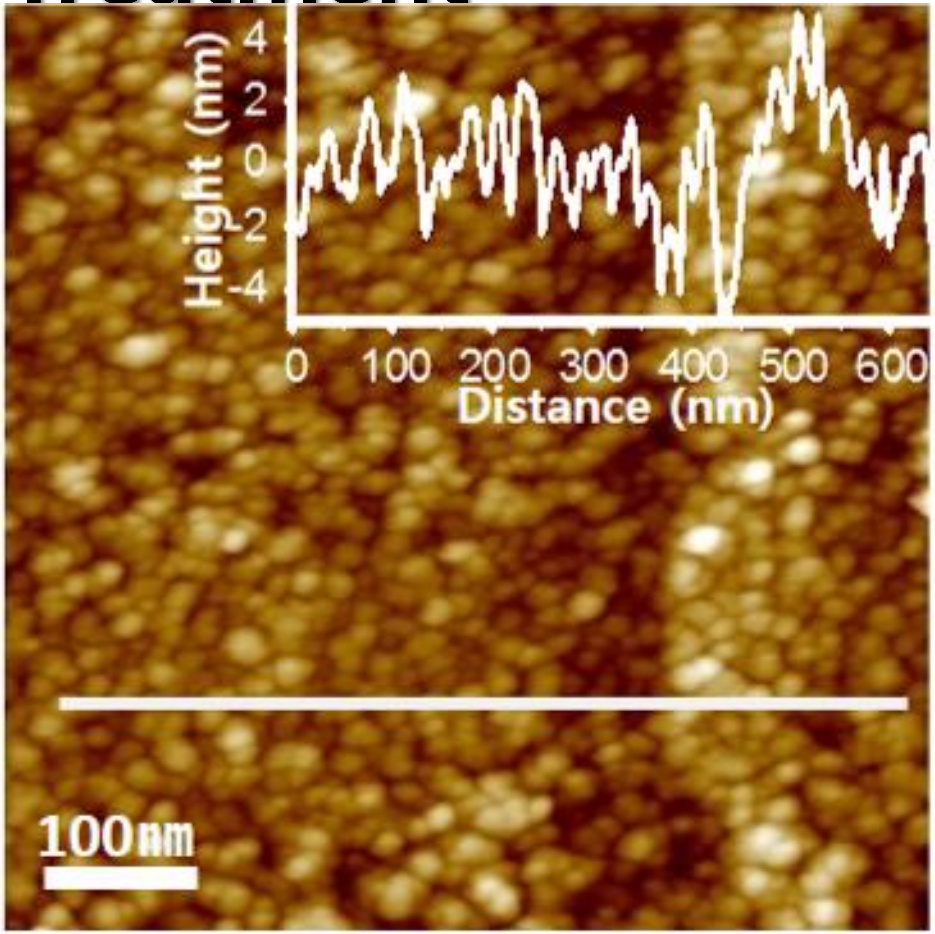


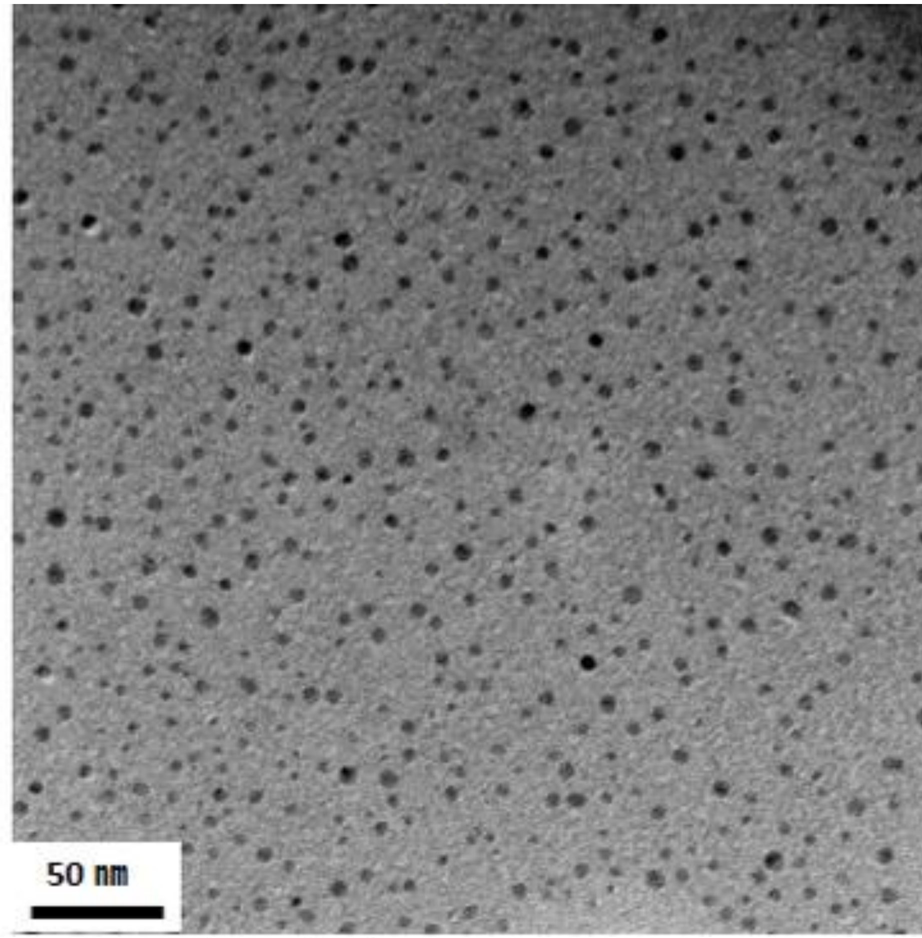
Transparent, catalytic, and "long-term stable"

Uk Sim et al., Energy Environ. Sci. (2013)

Doping Generation by N_2 Plasma Treatment

N-GQSs: N-doped graphene quantum sheets

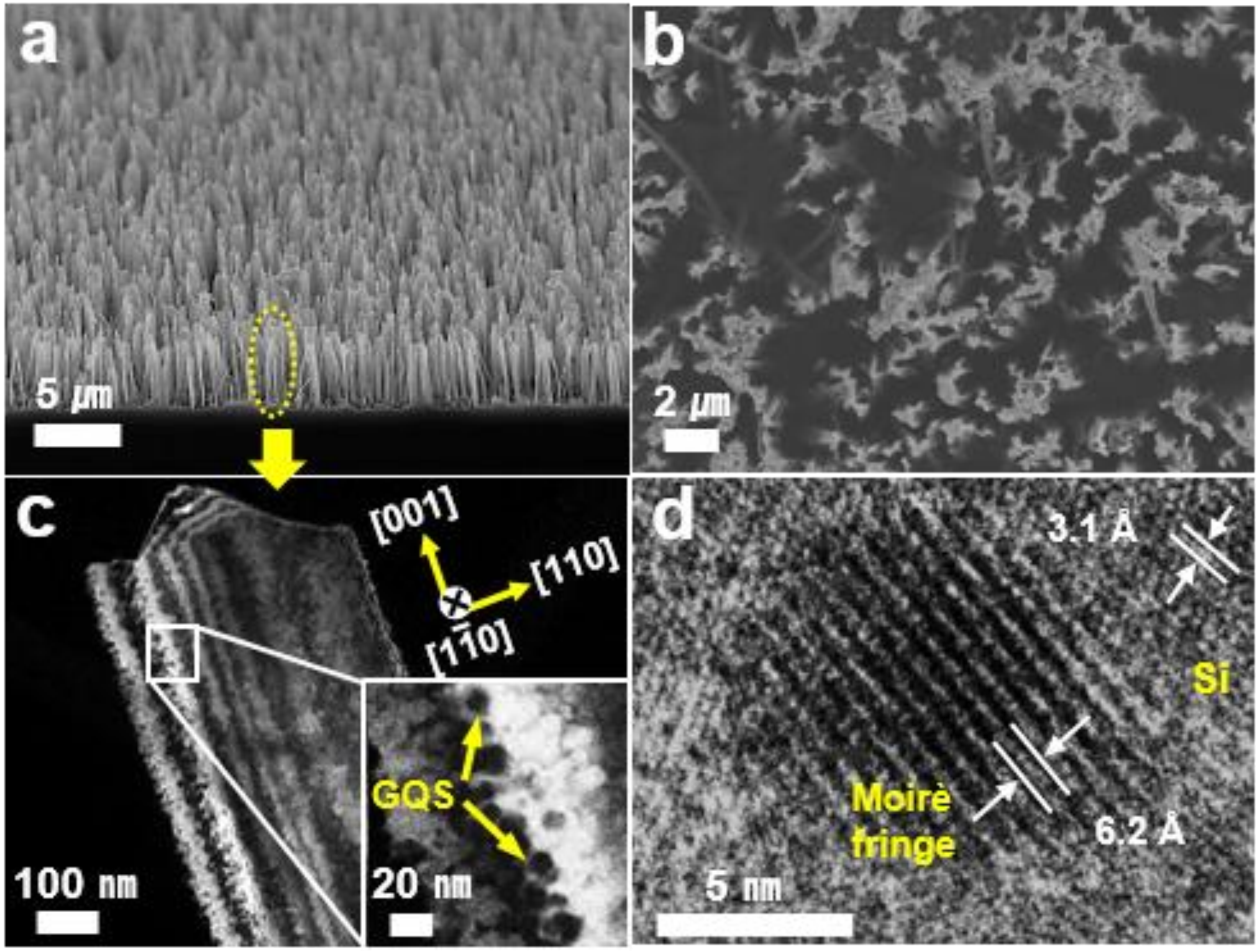


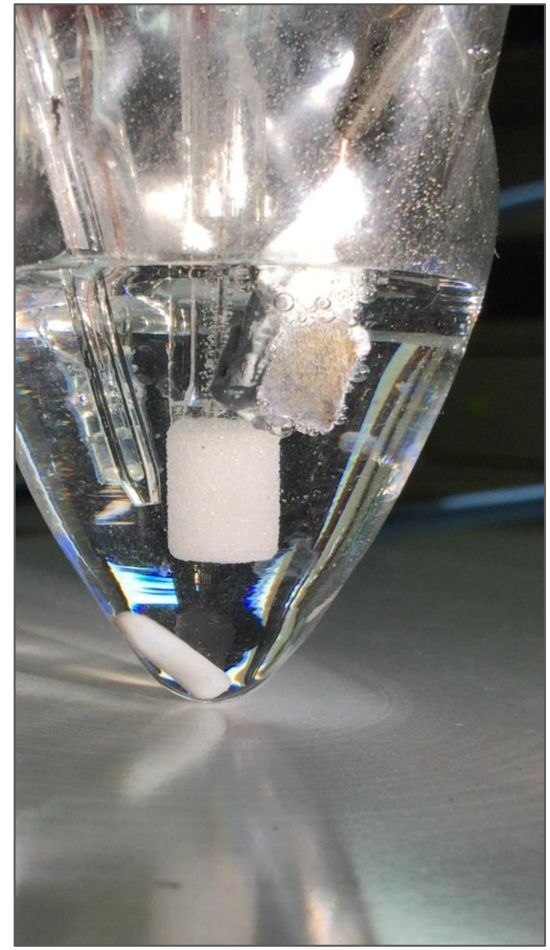


Increase of intrinsic active sites

*J. Moon., J. An, **U. Sim** et al., Adv. Mater. (2014)*
***Uk Sim** et al., Energy Environ. Sci. (2015)*
KR Patent (Registration: 10-1598017)

Optimized Interface Engineering

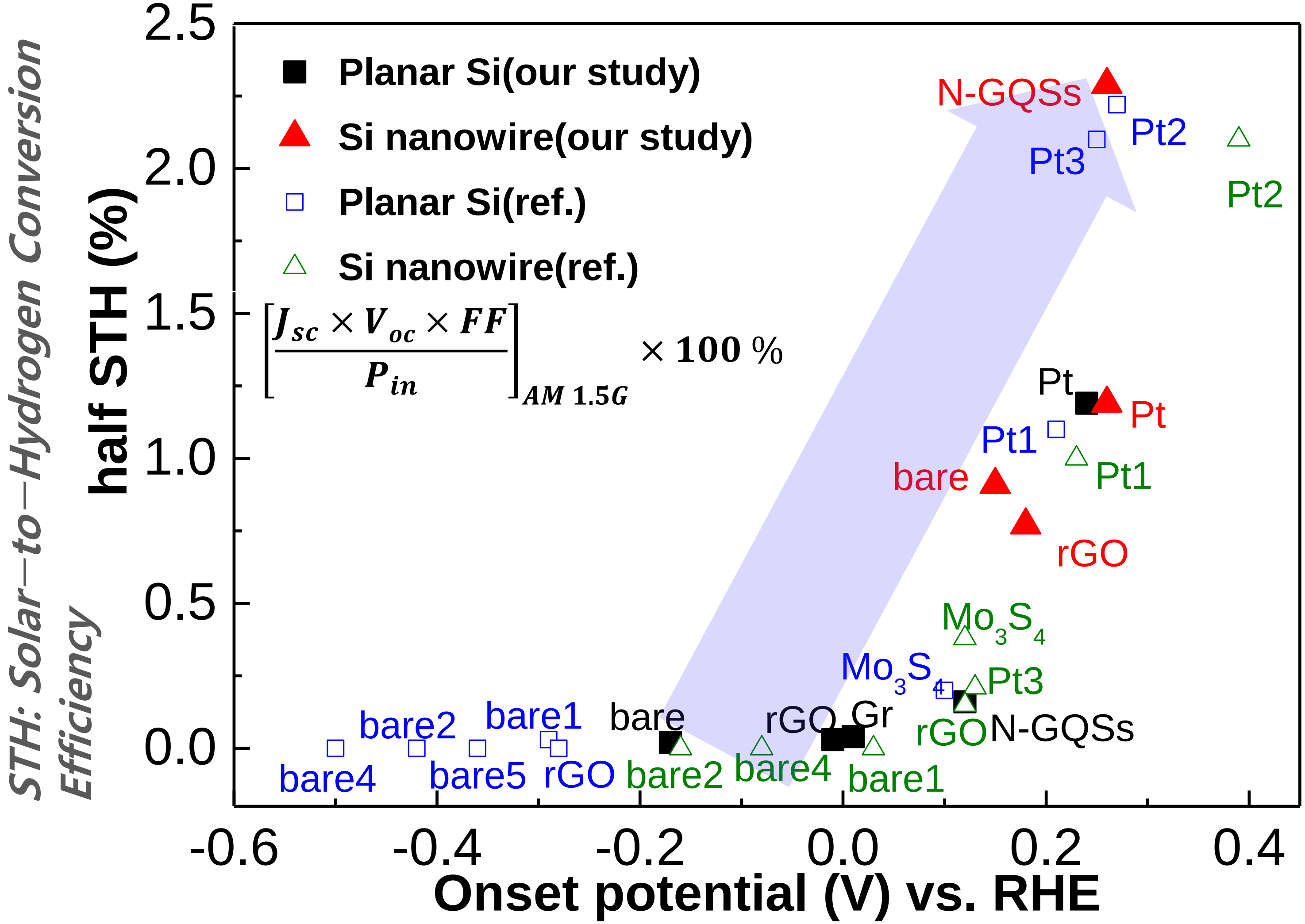




The spacing of Fringe,

$$a_m = (a_{GQS} \times a_{Si}) / \sqrt{a_{GQS}^2 + a_{Si}^2 - 2a_{GQS}a_{Si}\cos(\alpha_{GQS} - \alpha_{Si})}$$

Efficiency record

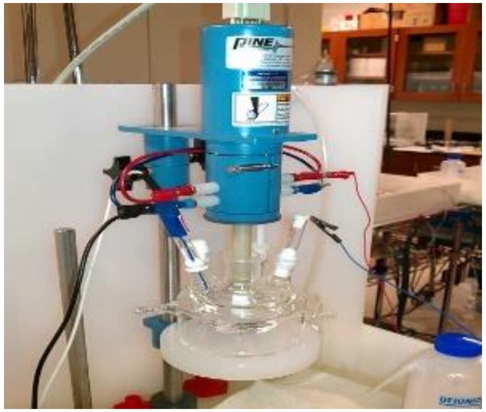


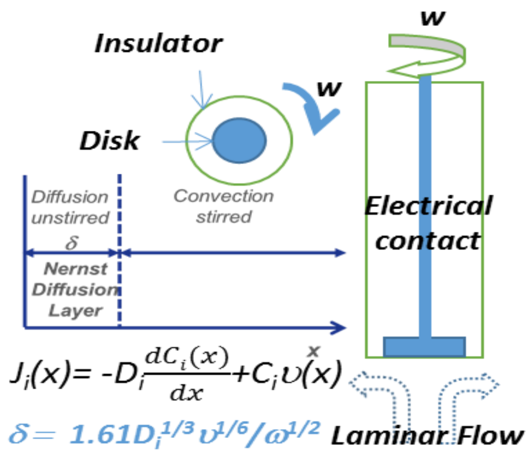
2.29%. Highest record among Si-based PEC cells

(450 times higher than bare Si and higher than Pt (2015)

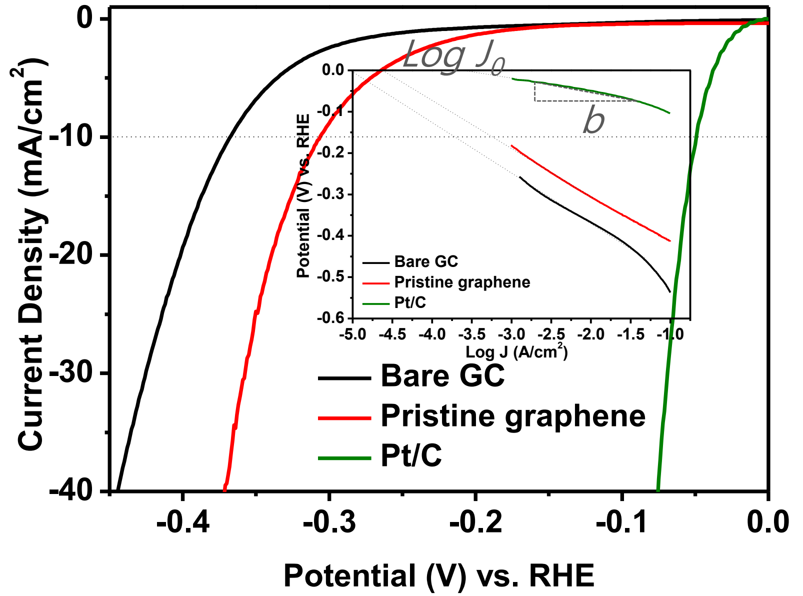
Electrochemical Response of Graphene

Rotating disk electrode





CV response and Tafel analysis



Hydrogen evolution reaction (HER)

(1) $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$ Discharge step *(Volmer reaction)*

(2) $H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O$ Electrochemical desorption step *(Heyrovsky reaction)*

(3) $H_{ads} + H_{ads} \rightarrow H_2$ Recombination step of adsorbed hydrogen *(Tafel reaction)*

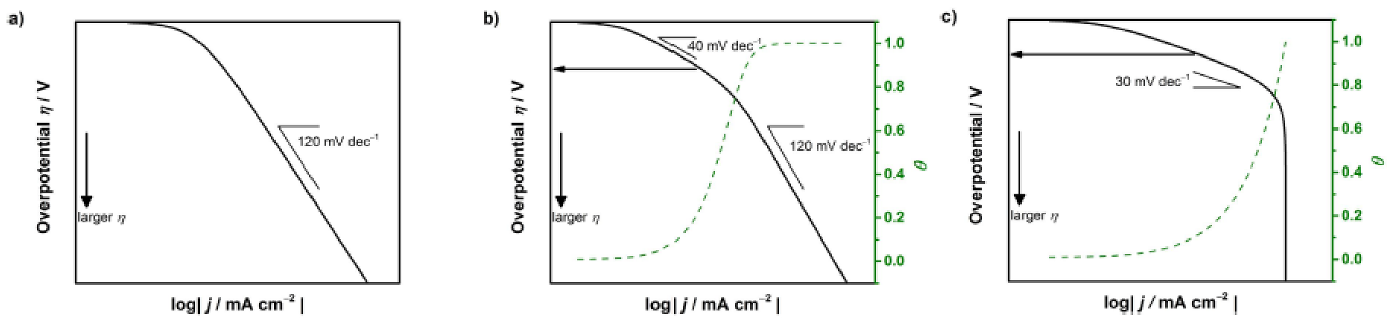
Rate determining step is,

- ***<u>Heyrovsky reaction:</u>*** $\theta_H \approx 0 \sim 1$: b = 40~118 mV/dec
- *Tafel reaction:* $\theta_H \approx 1$: b = 30 mV/dec

Uk Sim et al., Energy & Environ. Sci. **6**, 3658-3664 (2013)

Electrochemical Response of Graphene

Simulated behavior of the hydrogen evolution reaction



- **Forward reaction rate in Volmer reaction**

$\gamma = ka_{H_3O^+}(1-\theta)$ ········ (1)

$k = k^0 \exp(-\alpha f \eta)$ ········ (2)

$r = k^0 a_{H_3O^+} \exp(-\alpha f \eta)$ ········ (3)[(1)+(2)]

- **Electric current**

$I = nFAr$ ········ (4)

$I = nFAk^0 a_{H_3O^+} \exp(-\alpha f \eta)$ ········ (3)+(4)

- **Forward reaction rate in Heyrovsky reaction**

$\gamma = ka_{H_3O^+}\theta$

- **Electric current**

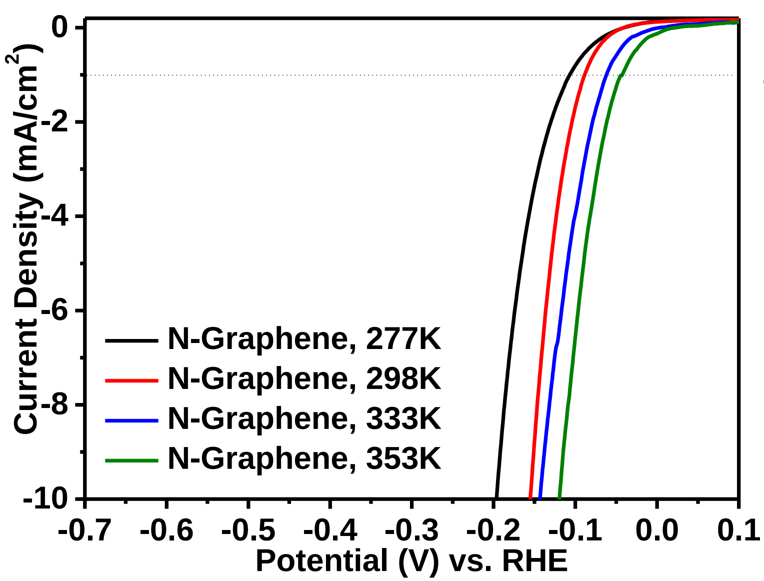
$$I = nFA \frac{k^0 a^2_{H_3O^+} \exp(-\alpha f \eta)}{a_{H_2O} \exp(f\eta) + k^0 a_{H_3O^+}}$$

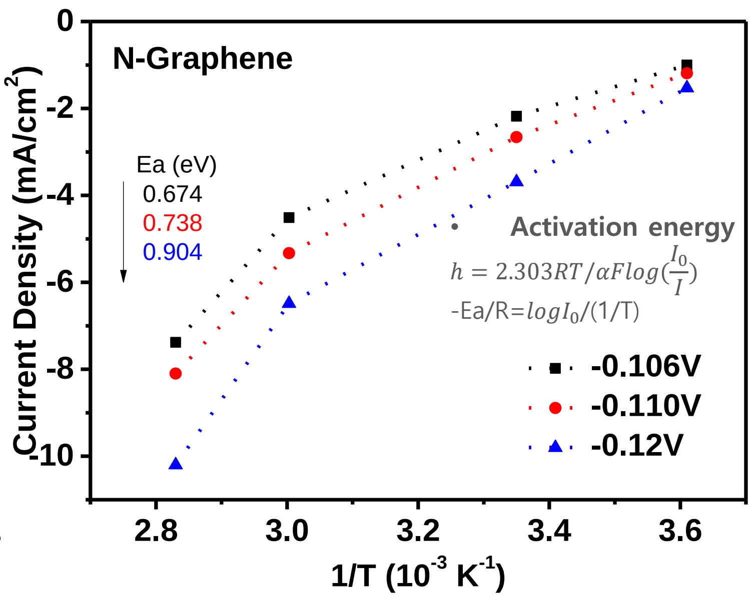
- **Forward reaction rate in Tafel reaction**

$\gamma = k^0 \theta^2$

- **Electric current**

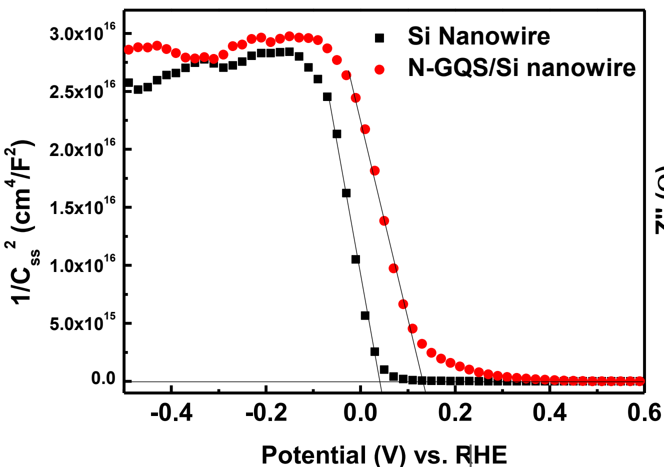
$$I = nFAk^0 \left[\frac{k^0 a_{H_3O^+}}{a_{H_2O} \exp(f\eta) + k^0 a_{H_3O^+}}\right]^2$$

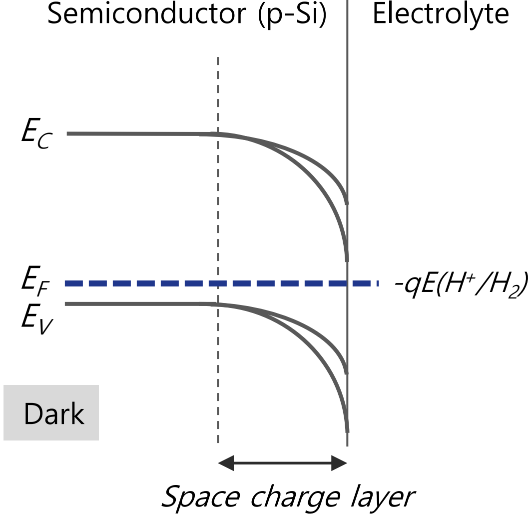




Interface analysis

Mott-Schottky Plot

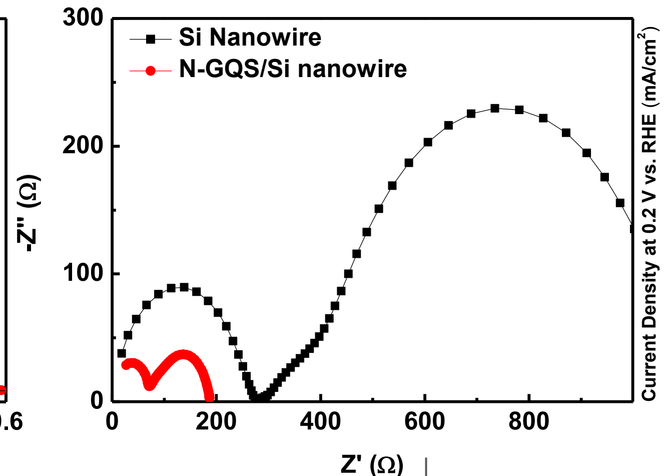


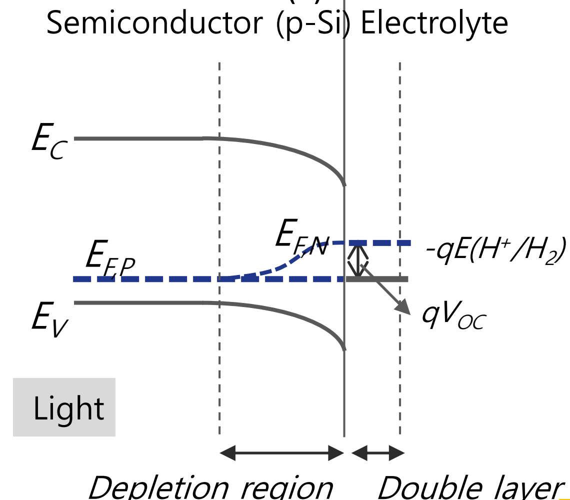


$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon_r \varepsilon_0 A^2 e N_{Dopant}}\left(E - E_{fb} - \frac{kT}{e}\right)$$

Higher band bending

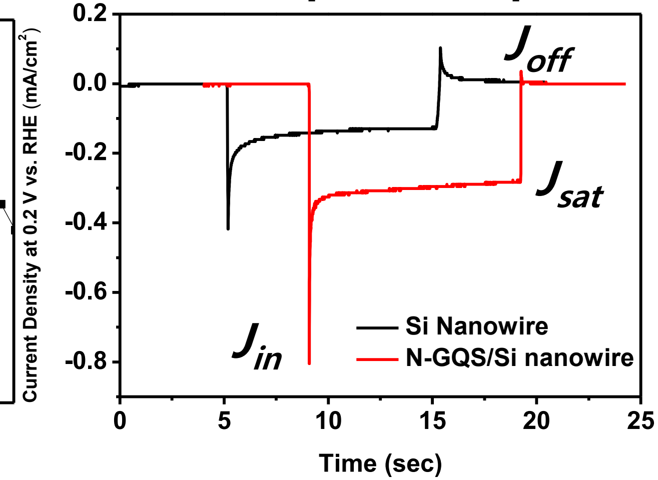
Nyquist plot





Lower charge transfer resistance

Transient photoresponse

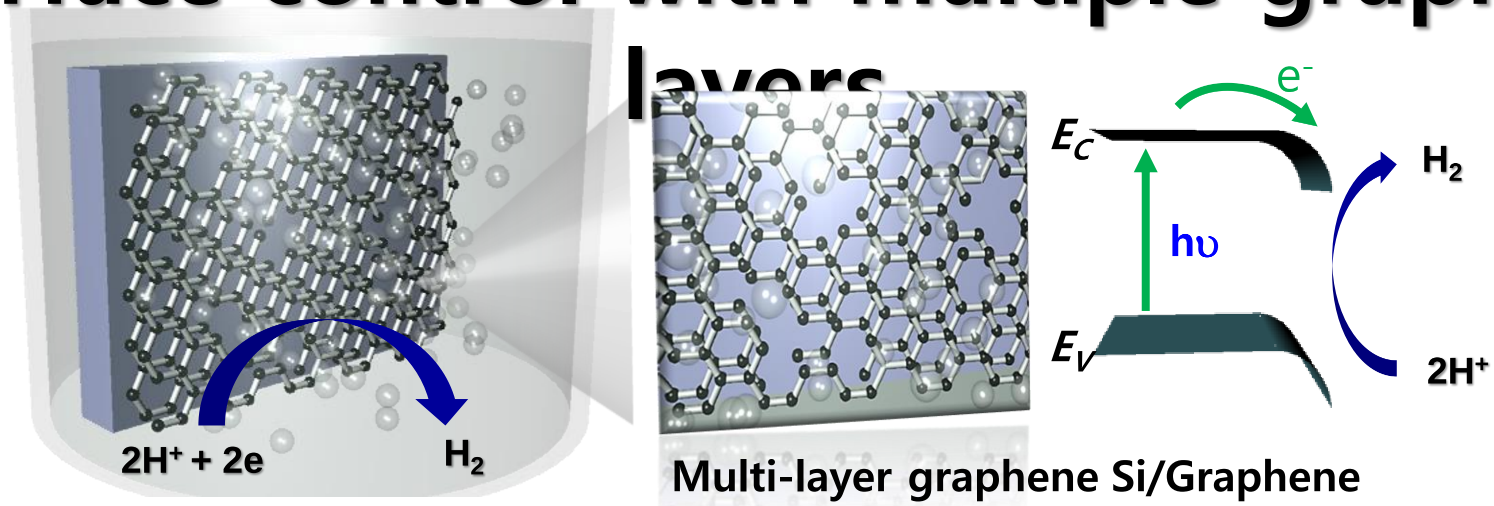


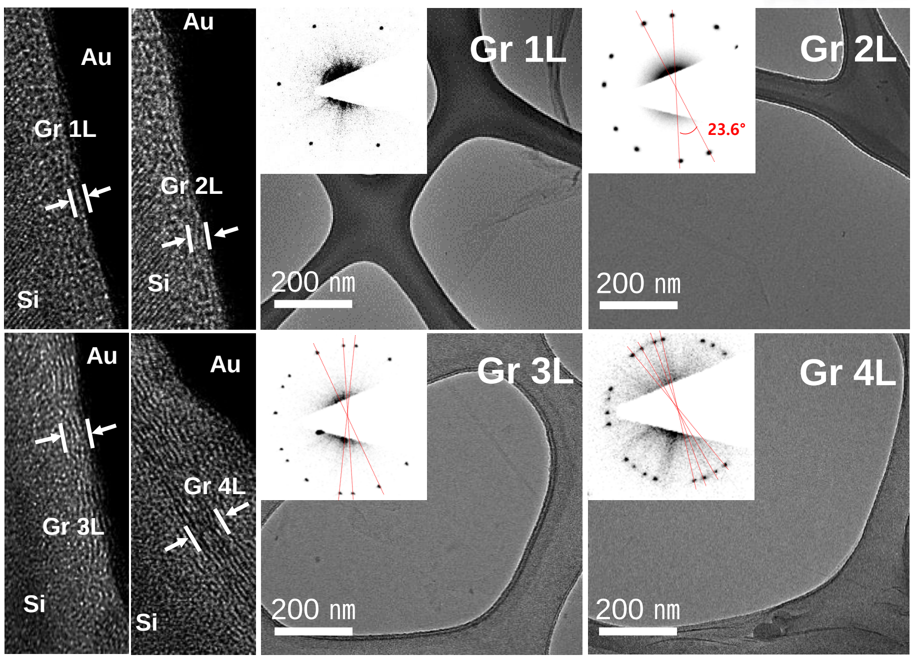
Higher J_{st}/J_{in} & lower J_{off}

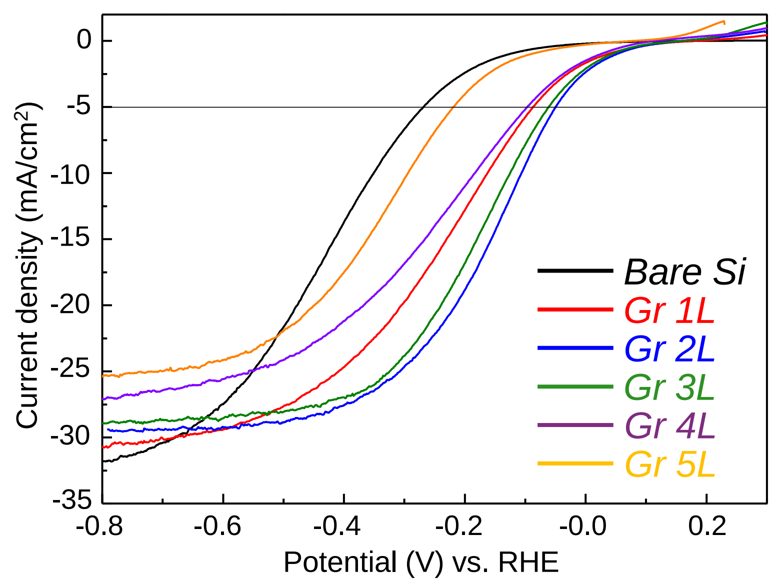
- **Fewer carriers trapped**
- **Less recombination**

Interface control: Lowering kinetic barriers & charge recombination

Interface control with multiple graphene layers





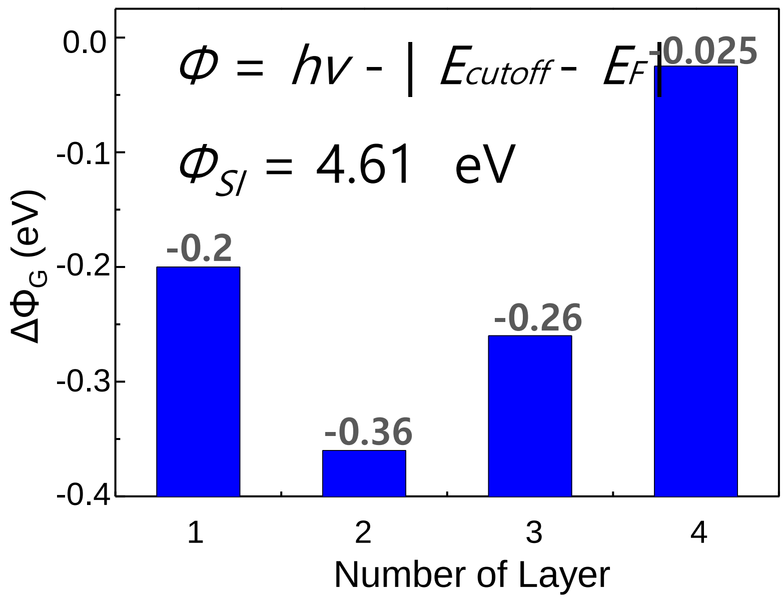


Systematic approach at the interface between electrode and electrolyte

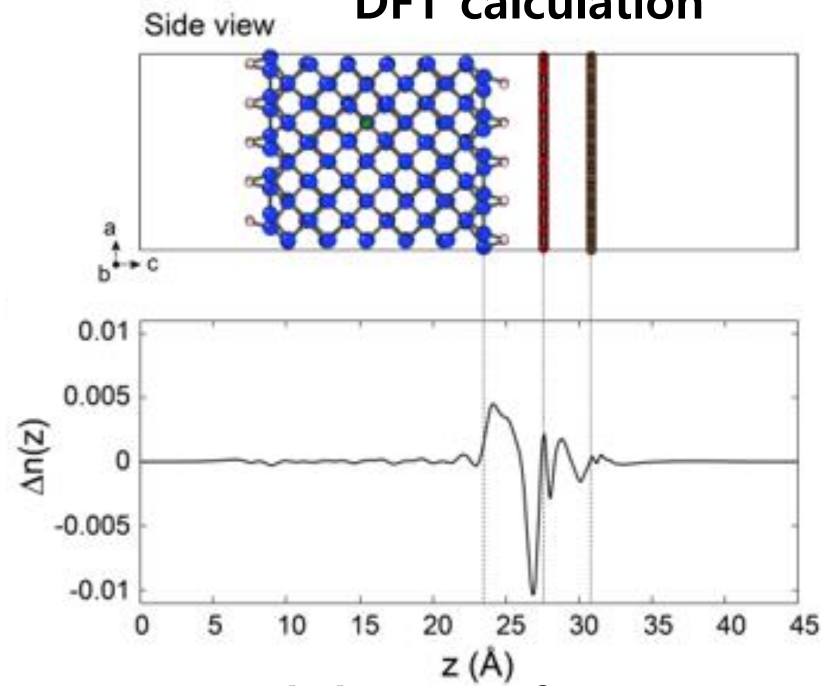
Uk Sim et al., ACS Appl. Mater. Inter. (2017)

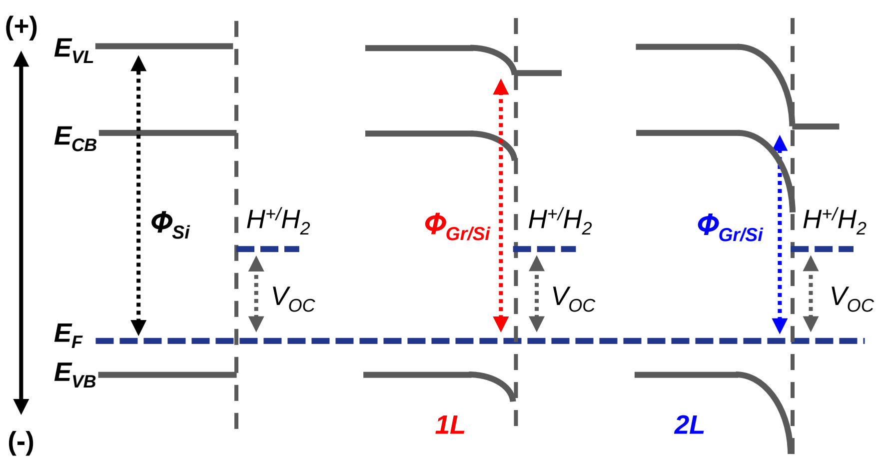
Mechanism at the interface

UPS measurement



DFT calculation



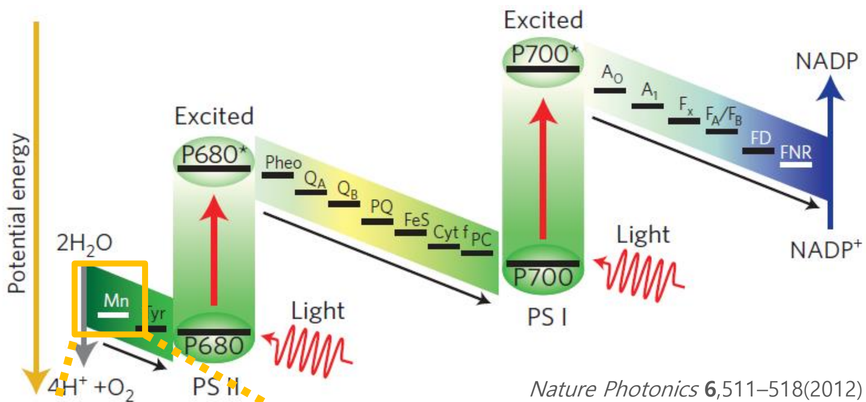


Increased density of states
→ Further Coulombic shift
→ The smallest work function
→ The highest band bend bending

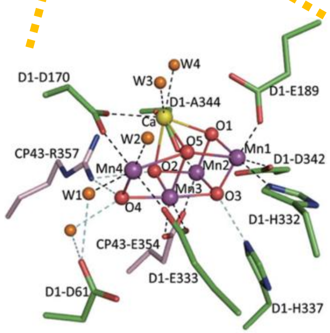
Importance of the electronic band structures of catalytic surface on photoelectrode

Natural enzyme

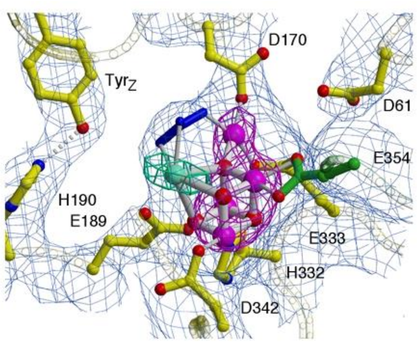
Oxygen Evolution



Nature Photonics **6**,511–518(2012)



Nature **473**, 55–60 (2011)

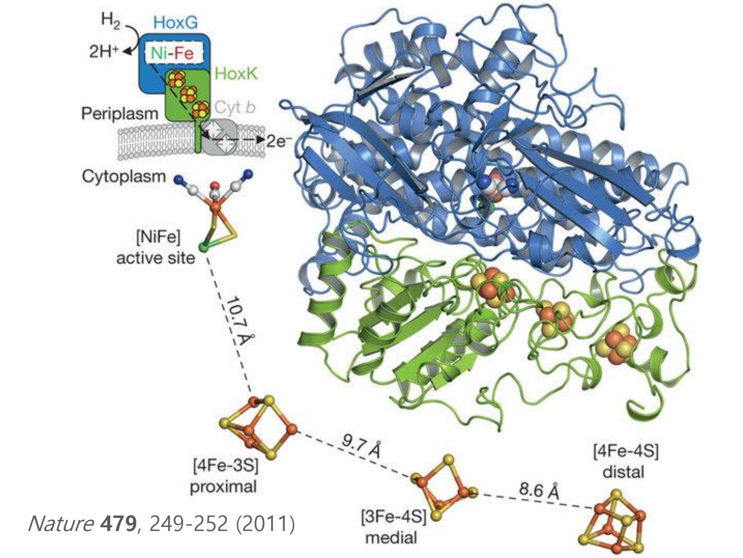


Science **303**, 1831-1838 (2004)

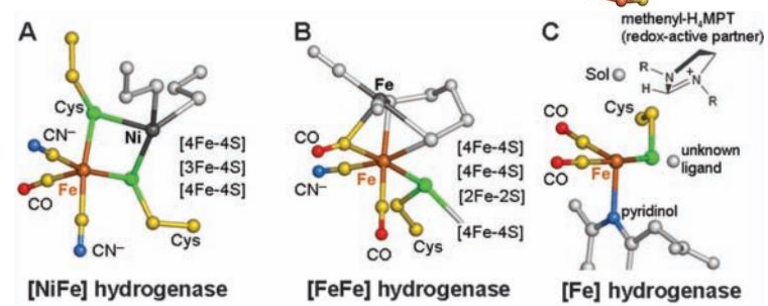
$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

PSII and Mn_4CaO_5 cluster

Hydrogen Evolution



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

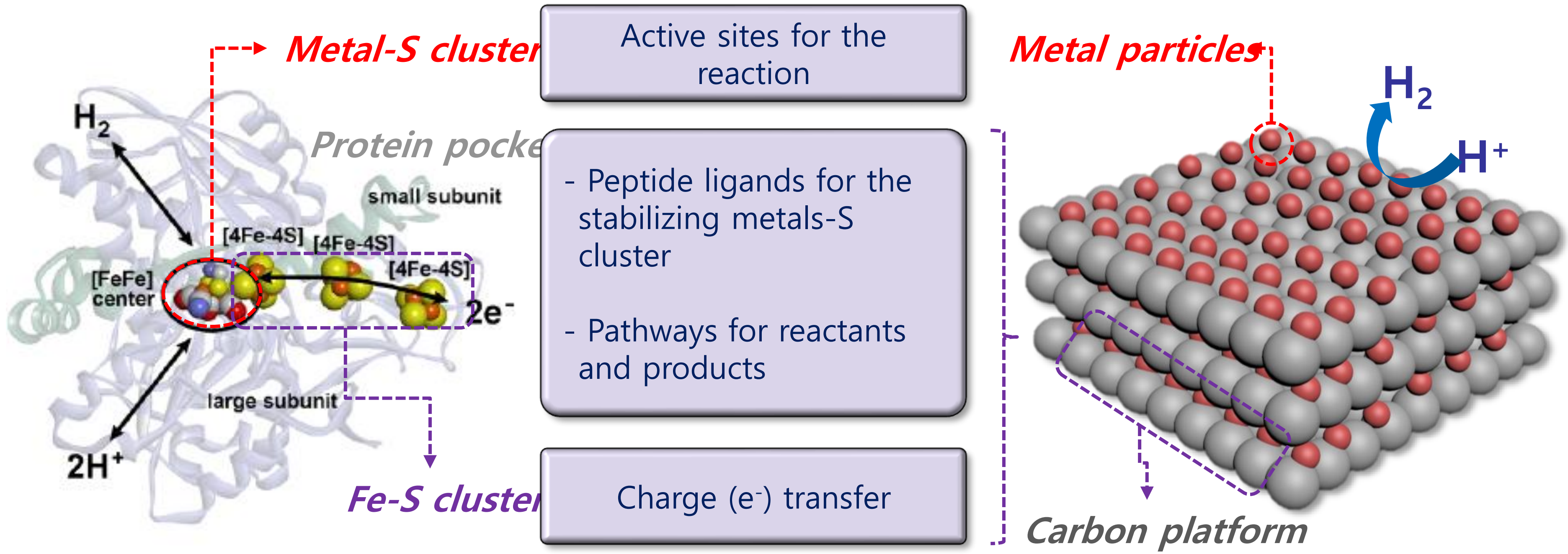


Science **321**, 572-575 (2008)

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

Hydrogenase and [Fe–S] cluster

Model System Study

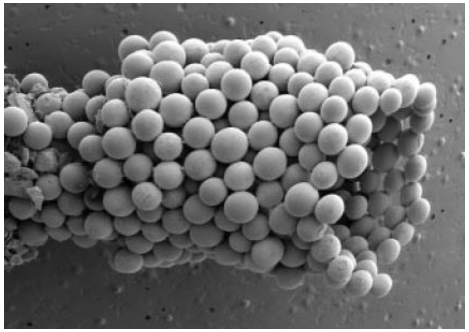


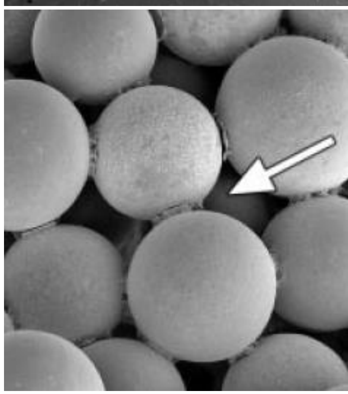
- ***Research direction of model system***

1. *Study of carbon platform: From 2D monolayer graphene to pseudo-3D system of multi-layer of graphene and graphene quantum sheets*
2. *Study of metal active sites: <u>Synthetic bioinspired carbon-based catalyst</u>*

Wet-resistance adhesives Found in Nature

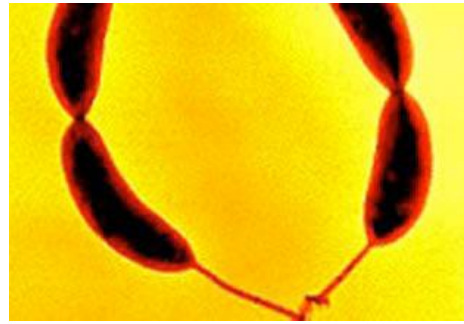
Tube-building polychaete



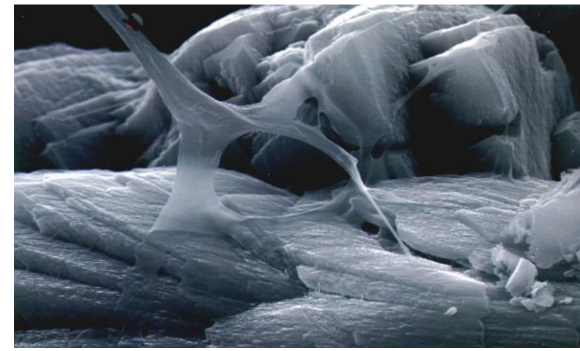


Barnacles

C. crescentus



Irish Moss, (C. crispus)

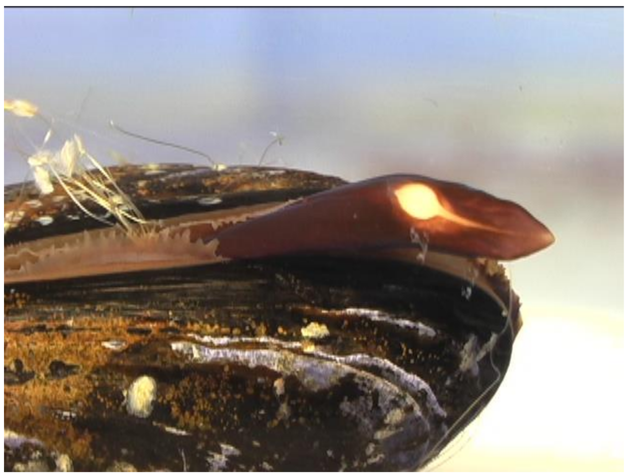


Biofilms

Mussels

Mussel Adhesion

Processes: molding → secretion → curing

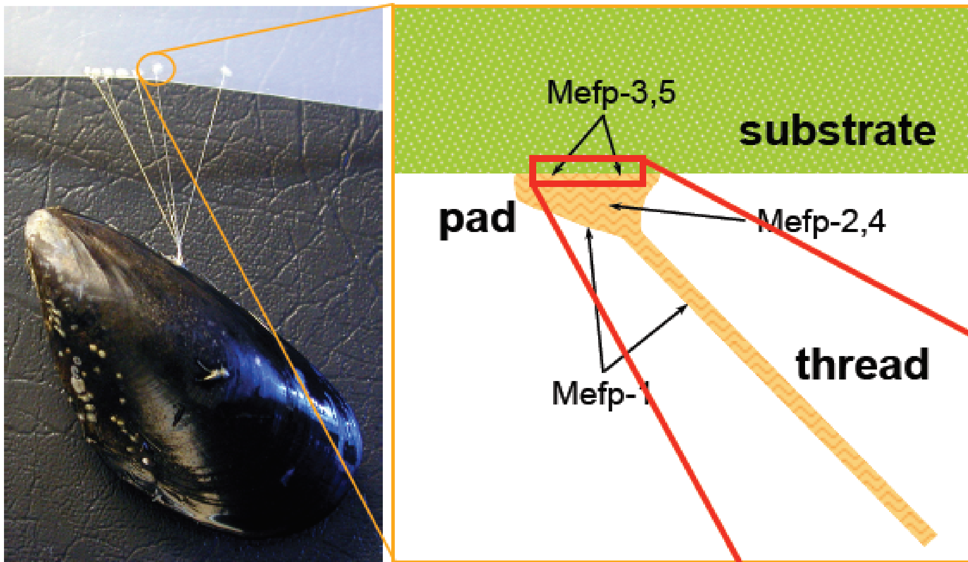


1. Water-resistant adhesion
2. Versatile adhesion

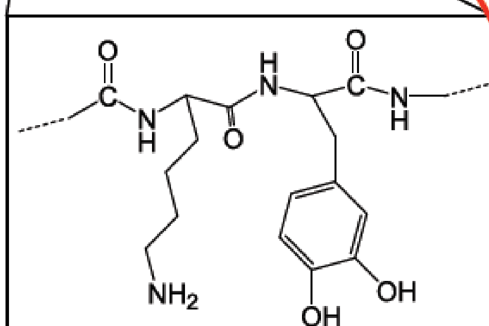
   Ship hull
   Rocks
   Water plant leaves
   Feathers
   Fish skin
   Drinking bottles
   Teflon®

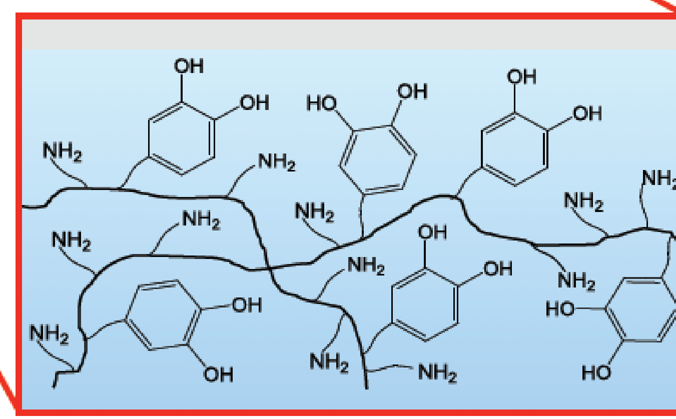
https://youtu.be/dPgzSHe9fg8

Mussel adhesion : DOPA-Lys Motif



Mefp5[1]
1 SSEEYKGGYYPGNAYHYHSGGSYHG
26 SGYHGGYKGKYYGKAKKYYYKYKNS
51 GKYKYLKKARKYHRKGYKYYGGSS
Mefp3[2]
1 ADYYGPNYGPPRRYGGGNYNRYNRY
26 GRRYGGYKGWNNGWNRGRRGKYW

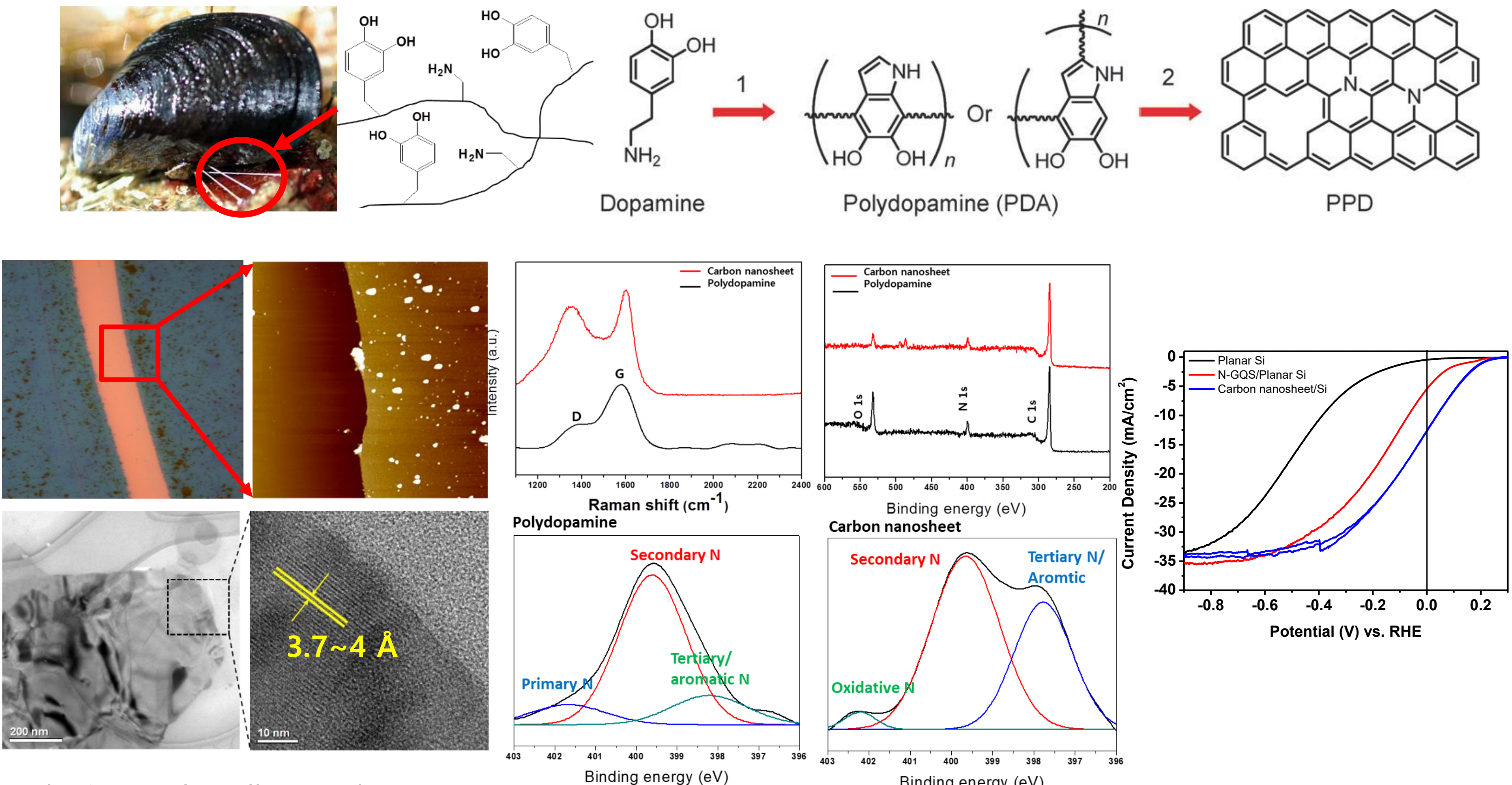




Y: DOPA

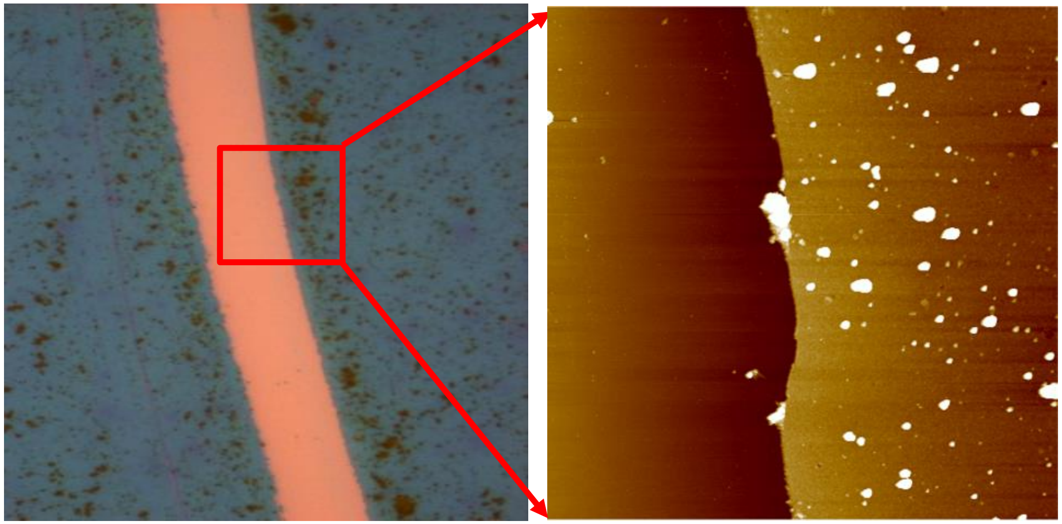
Synthetic Bioinspired Carbon-based Catalyst

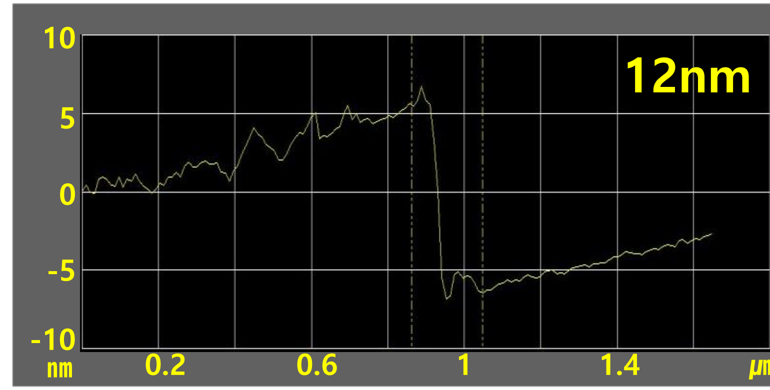
Poly(dopamine): Adhesive proteins secreted by marine mussels

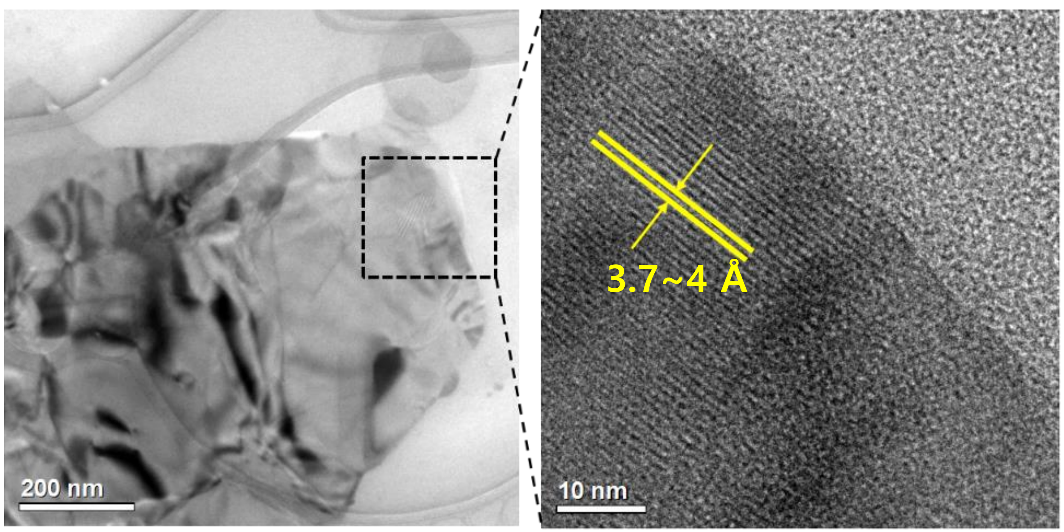


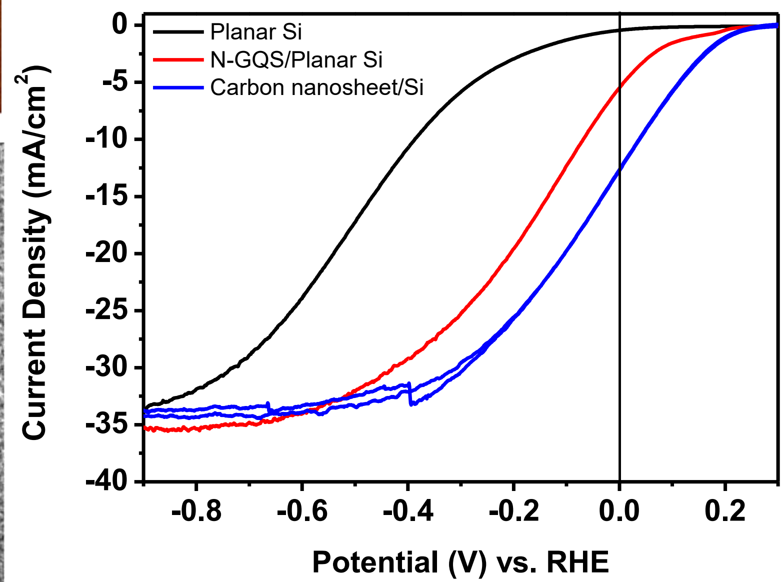
Uk Sim et al., Bull. Kor. Chem. Soc. (2018)

Characterization of Carbon Nanosheet









	ABPE (%)
Planar Si	0.02
N-GQSs	0.16
Carbon nanosheet	**0.59**

Uk Sim et al., Bull. Kor. Chem. Soc. (2018)