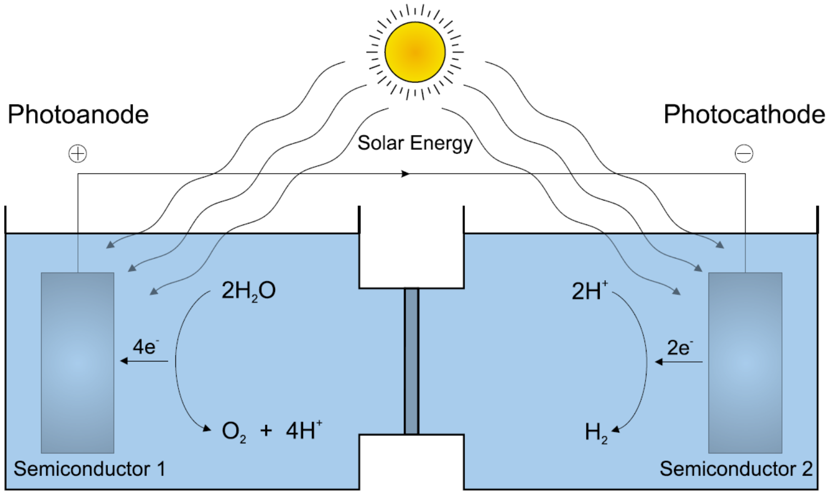
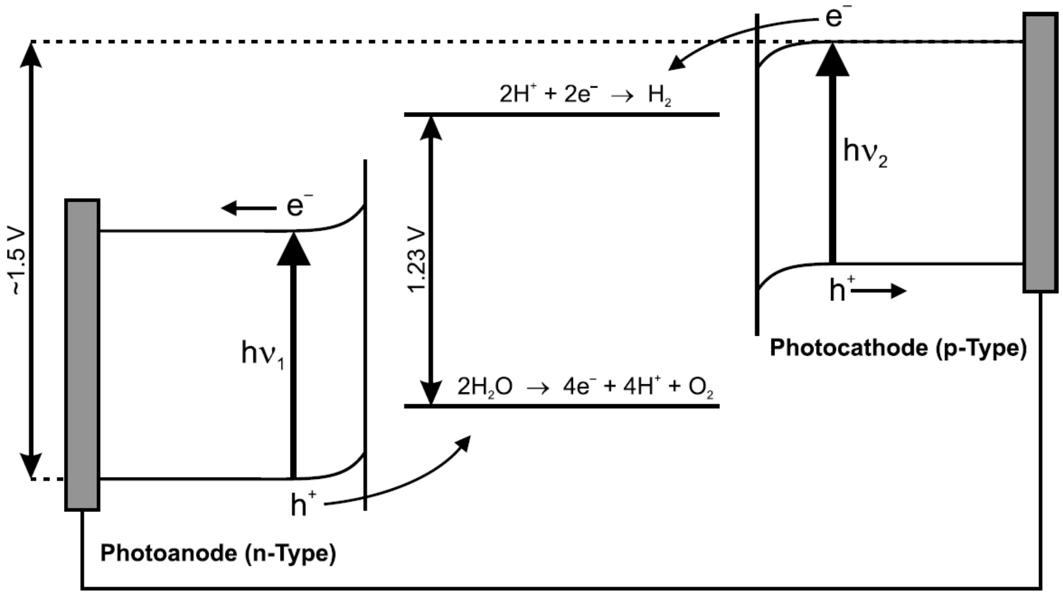
광전기화학 시스템 광전극 소재 설계

Design of Photoelectrodes

Uk Sim
Department of Materials Science & Engineering
Chonnam National University

Water Splitting Reaction at Semiconductor/Liquid Junction





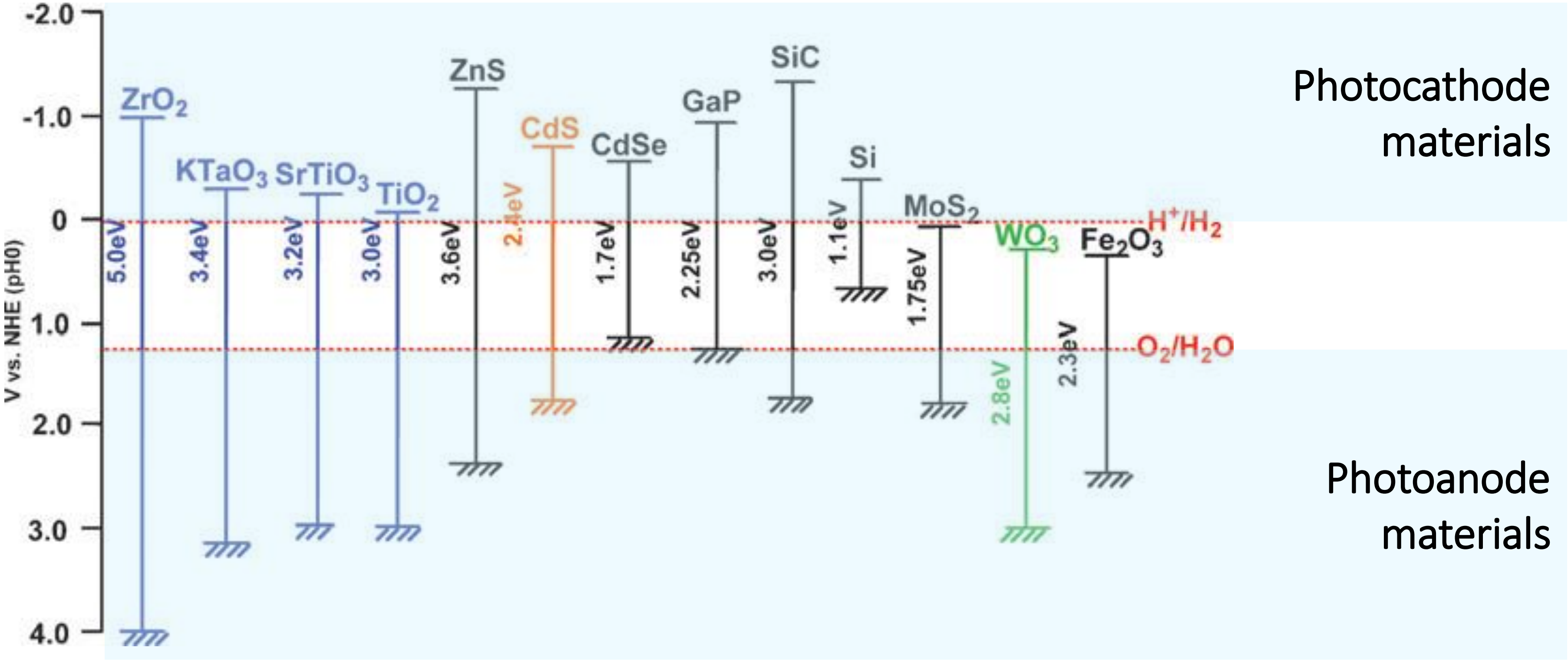
$H_2O + 2h^+ \rightarrow \frac{1}{2} O_2 + 2H^+$ $E_{anodic} = 1.23\ V - 0.059(pH)\ V(NHE)$

$2H^+ + 2e^- \rightarrow H_2$ $E_{cathodic} = 0\ V - 0.059(pH)\ V(NHE)$

$H_2O \rightarrow H_2 + \frac{1}{2} O_2$ $\Delta G_0 = 237\ kJ/mol\ (\Delta E_0 = -1.23V)$

CHIMIA **2007**, *61*, 12

Band structures and Redox potentials



Photocathode
materials

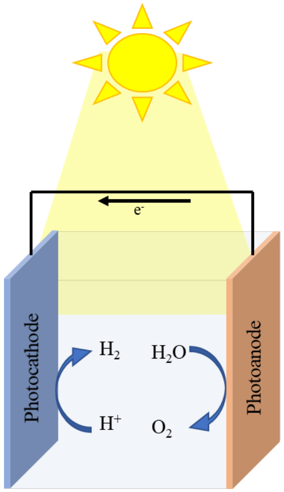
Photoanode
materials

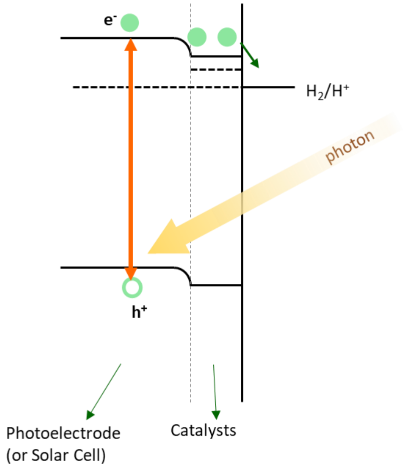
Akihiko Kudo and Yugo Miseki, Chem. Soc. Rev., **38**, 253,

Photoelectrochemical

Unassisted System

➢ Unassisted System (Tandem Cell)

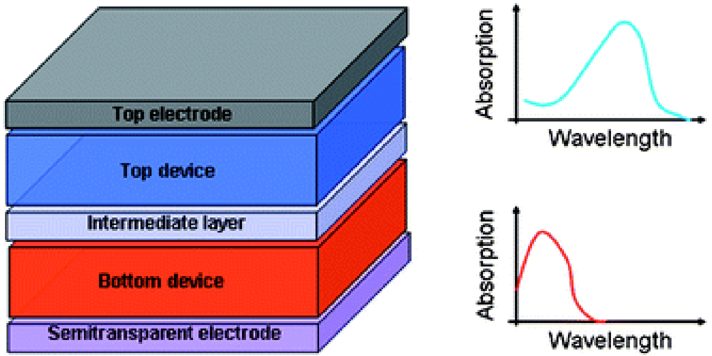




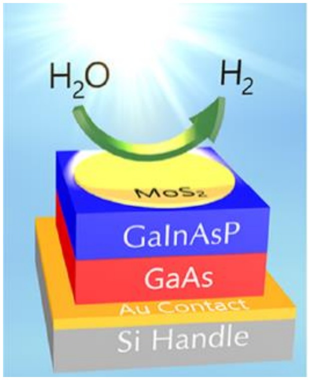
Photoelectrode / Solar Cell + Catalysts

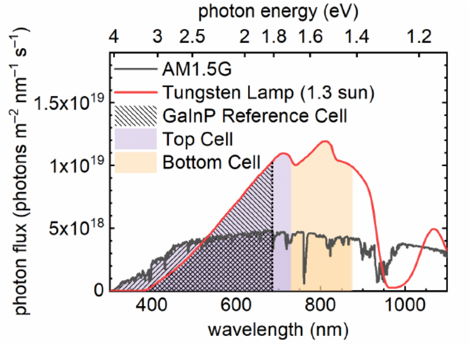
- Generates electrical current to operate the cell
- Generates EHP for the catalyst to cause redox reaction

Tandem Cell are device with two or more materials with different bandgap; usually used in solar cells



Top cell with narrow bandgap, bottom cell with wider;
Allowing to absorb more photons and reduce recombination rate





Energetics of Semiconductor/Liquid Junctions under Illumination

The photovoltage (Voc) generated at a semiconductor/liquid junction

$$V_{\rm oc} = (nk_{\rm B}T/q)\ln(J_{\rm ph}/\gamma J_{\rm s})$$

n: the diode quality factor
Jph (A m^{-2}): the photocurrent density,
Js : the saturation current density, which is related to the sum of the recombination pathways
γ: the ratio of the actual junction area to the geometric surface of the electrode (i.e., the roughness factor)

The electron concentration at the surface of an n-type semiconductor, n_s,

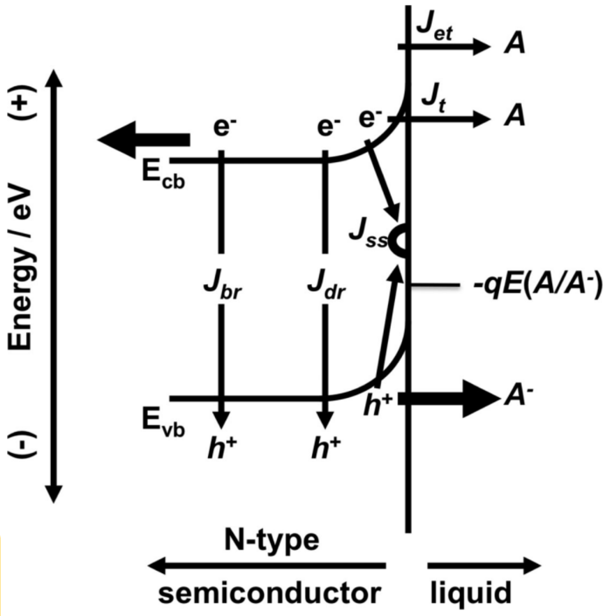
$$n_{\rm s} = N_{\rm d}e^{q(E_{\rm fb}-E)/k_{\rm B}T}$$

E_{fb}: the flat-band potential,
N_d: the concentration of donor atoms

The net flux of electrons from the conduction band to acceptors dissolved in solution

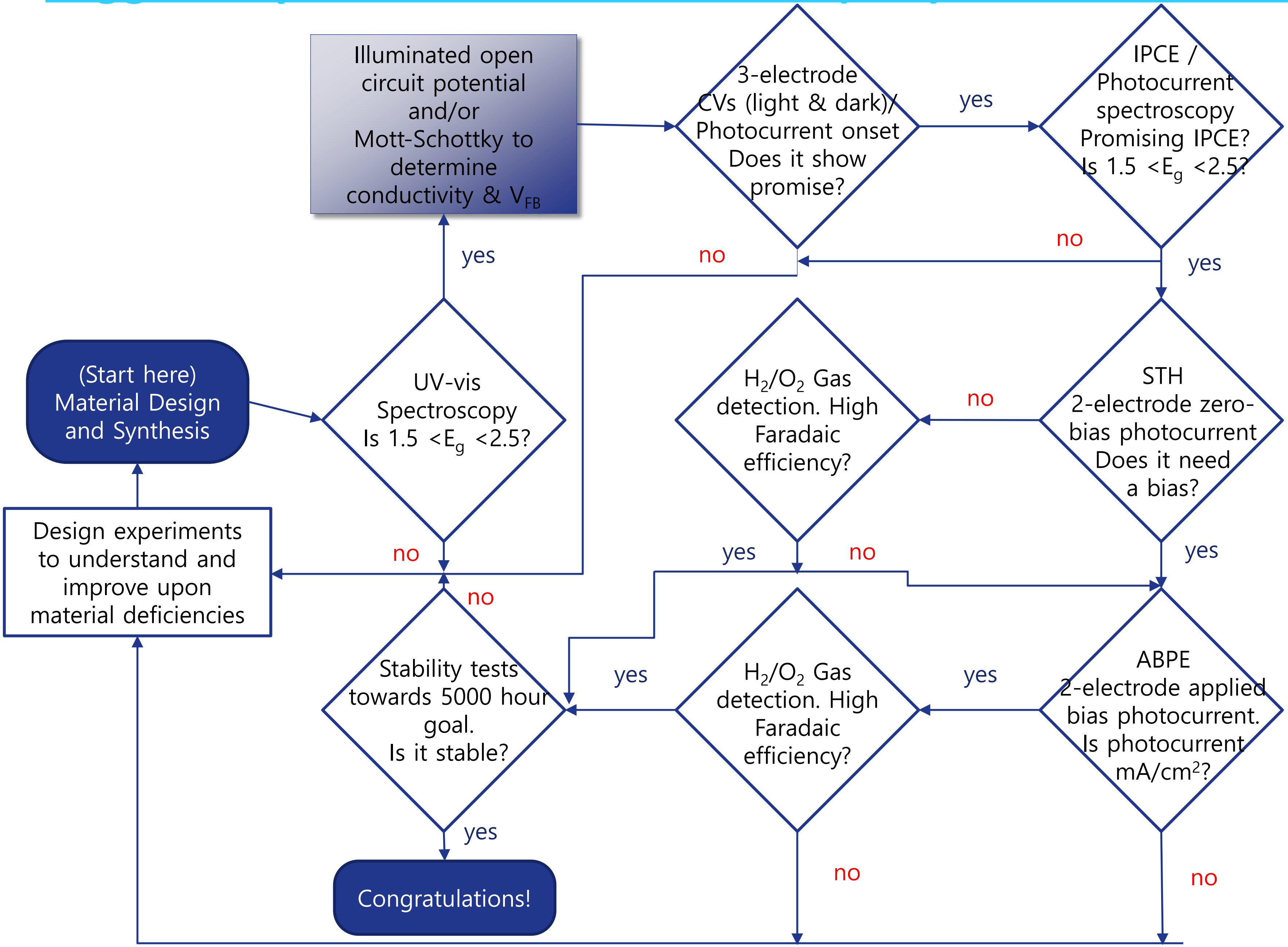
$$J(E) = -qk_{\rm et}[{\rm A}]n_{\rm s}$$

J is the current density (A cm-2),
k_{et} is the electrontransfer rate constant (cm4 s-1),
[A] is the acceptor concentration (cm-3)



J_{br}: radiative or nonradiative recombination in the bulk of the semiconductor,
J_{dr}: depletion-region recombination,
J_{ss}: surface recombination due to defects,
J_t: tunneling current,
J_{et}: electron-transfer current associated with majority carriers traversing the interfacial barrier
.

Suggested photoelectrochemical cell (PEC) characterization



(Start here)
Material Design and Synthesis

UV-vis Spectroscopy
Is 1.5 <E_g <2.5?

Illuminated open circuit potential and/or Mott-Schottky to determine conductivity & V_{FB}

3-electrode CVs (light & dark)/ Photocurrent onset
Does it show promise?

IPCE / Photocurrent spectroscopy
Promising IPCE?
Is 1.5 <E_g <2.5?

STH
2-electrode zero-bias photocurrent
Does it need a bias?

H_2/O_2 Gas detection. High Faradaic efficiency?

ABPE
2-electrode applied bias photocurrent.
Is photocurrent mA/cm^2?

H_2/O_2 Gas detection. High Faradaic efficiency?

Stability tests towards 5000 hour goal.
Is it stable?

Congratulations!

Design experiments to understand and improve upon material deficiencies

Primary measurments of efficieny

(i) Benchmark efficiency (suitable for mainstream reporting)
- (a) solar-to-hydrogen conversion efficiency (STH)

(ii) Diagnostic efficiencies (to understand material performance)
- (a) applied bias photon-to-current efficiency (ABPE)
- (b) external quantum efficiency (EQE) = incident photon-to-current efficiency (IPCE)
- (c) internal quantum efficiency (IQE) = absorbed photon-to-current efficiency (APCE).

$$\mathrm{STH} = \left[\frac{(\mathrm{mmol\,H_2/s}) \times (237\ \mathrm{kJ/mol})}{P_{\mathrm{total}}(\mathrm{mW/cm^2}) \times \mathrm{Area}\ (\mathrm{cm^2})}\right]_{\mathrm{AM\,1.5\,G}} \qquad \mathrm{STH} = \left[\frac{\left|j_{SC}(\mathrm{mA/cm^2})\right| \times (1.23\mathrm{V}) \times \eta_F}{P_{\mathrm{total}}(\mathrm{mW/cm^2})}\right]_{\mathrm{AM\,1.5\,G}}$$

$$\mathrm{ABPE} = \left[\frac{\left|j_{ph}(\mathrm{mA/cm^2})\right| \times (1.23 - |V_b|)(\mathrm{V})}{P_{\mathrm{total}}(\mathrm{mW/cm^2})}\right]_{\mathrm{AM\,1.5\,G}}$$

$$\mathrm{IPCE} = \mathrm{EQE} = \eta_{\mathrm{e^-/h^+}}\eta_{\mathrm{transport}}\eta_{\mathrm{interface}}$$

$$\mathrm{IPCE}(\lambda) = \mathrm{EQE}(\lambda) = \frac{\mathrm{electrons/cm^2/s}}{\mathrm{photons/cm^2/s}} = \frac{\left|j_{ph}(\mathrm{mA/cm^2})\right| \times 1239.8(\mathrm{V} \times \mathrm{nm})}{P_{\mathrm{mono}}(\mathrm{mW/cm^2}) \times \lambda(\mathrm{nm})}$$

$\eta_{e-/h+}$: Photon absorptance (the fraction of electron-hole pairs generated per incident photon flux)

$\eta_{\mathrm{transport}}$:Charge transport to the solid-liquid interface

$\eta_{\mathrm{interface}}$:The efficiency of interfacial charge transfer

$$\mathrm{APCE} = \mathrm{IQE} = \frac{\mathrm{IPCE}}{\eta_{\mathrm{e^-/h^+}}} = \eta_{\mathrm{transport}}\eta_{\mathrm{interface}}$$

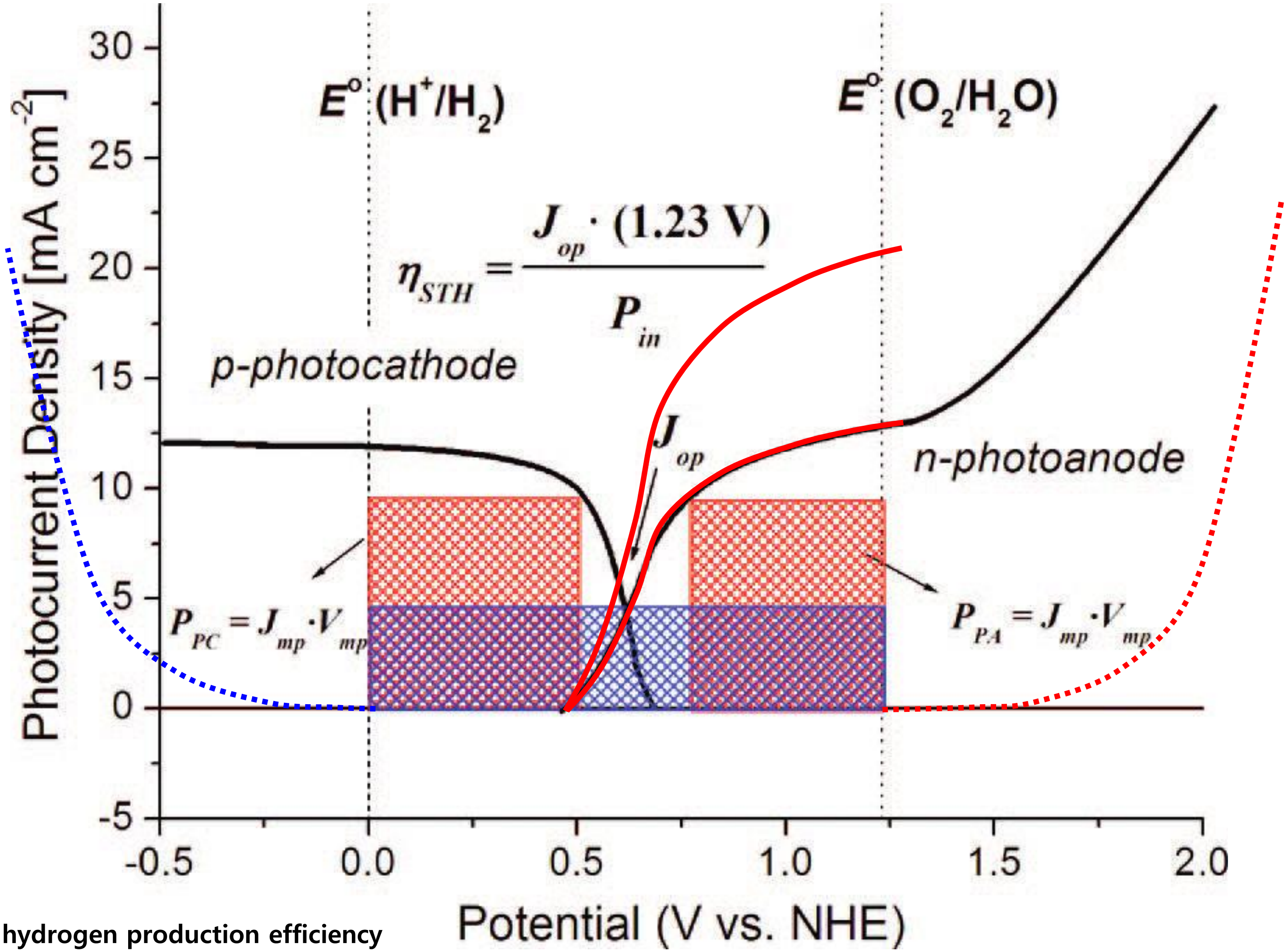
$$\mathrm{APCE}(\lambda) = \mathrm{IQE}(\lambda) = \frac{\left|j_{ph}(\mathrm{mA/cm^2})\right| \times 1239.8(\mathrm{V} \times \mathrm{nm})}{P_{\mathrm{mono}}(\mathrm{mW/cm^2}) \times \lambda(\mathrm{nm}) \times (1 - 10^{-A})}$$

$$A = -\log\left(\frac{I}{I_0}\right),$$

$$\eta_{\mathrm{e^-/h^+}} = \frac{I_0 - I}{I_0} = 1 - \frac{I}{I_0} = 1 - 10^{-A}$$

Overall Water Splitting Efficiency

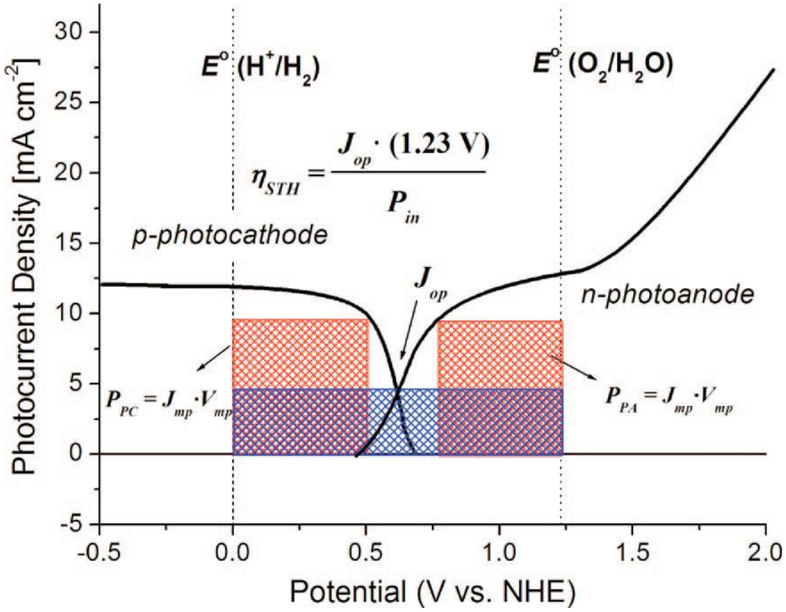
M. G. Walter *et al.*, *Chem. Rev*. **110**, 6446 (2010)



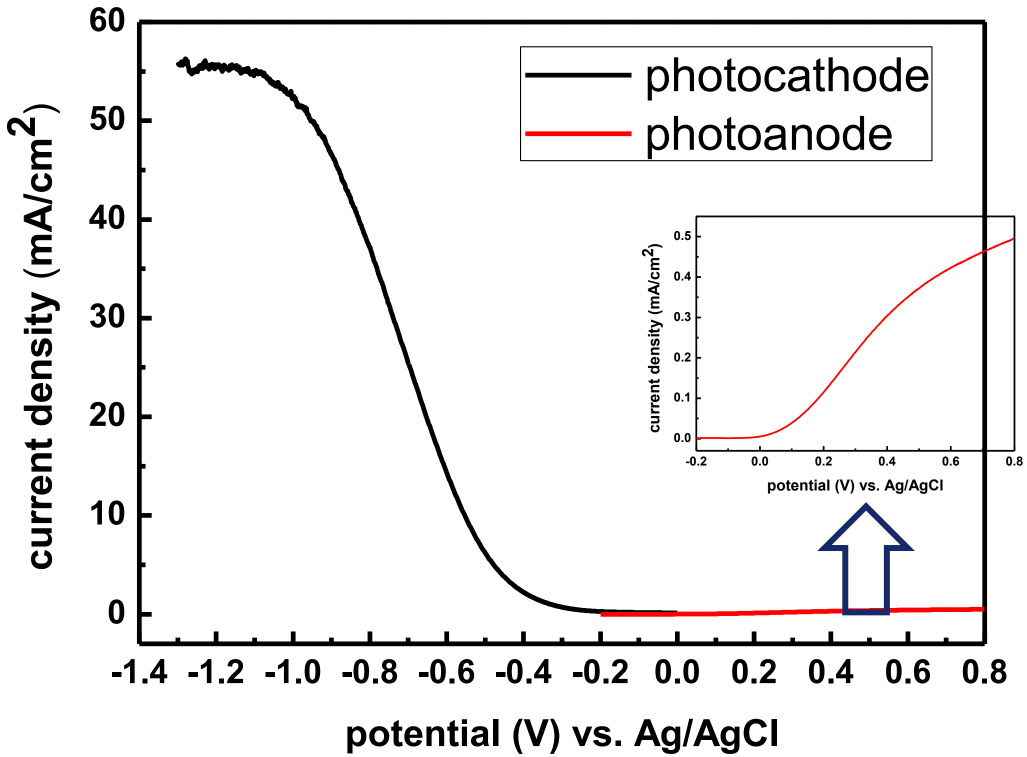
η_{STH} : true solar to hydrogen production efficiency
V_{app}: the applied voltage measured between the photoanode and the photocathode
J_{mp}: the externally measured current density
P_{in}: the power density of the illumination

Overall Water Splitting Efficiency

Theoretically,



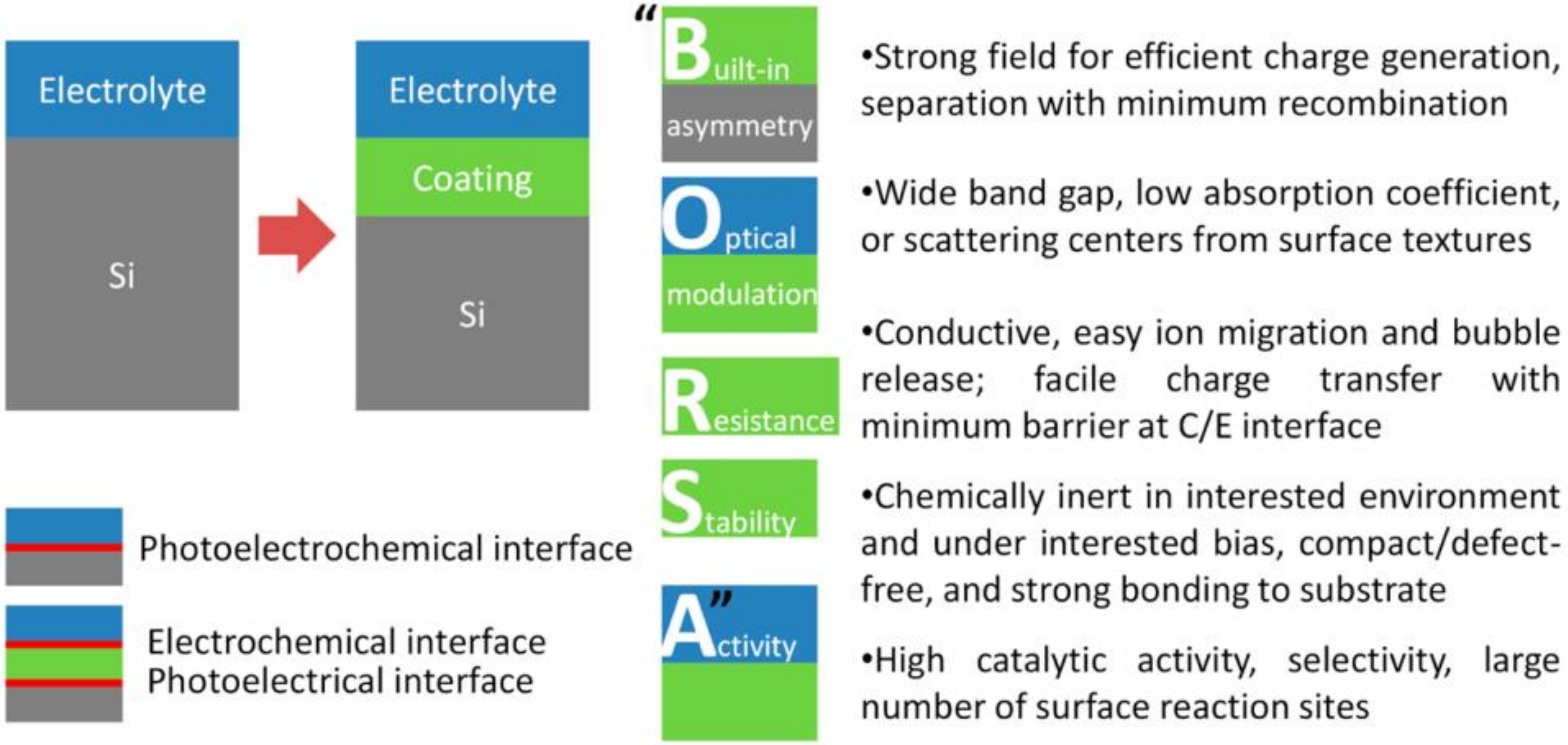
In real,



η_{STH} : true solar to hydrogen production efficiency
V_{app}: the applied voltage measured between the photoanode and the photocathode
J_{mp}: the externally measured current density
P_{in}: the power density of the illumination

Chem. Rev., 110, 2010, 5449

“BORSA” : Consideration of photoelectrochemical system design



“**B**uilt-in asymmetry

- Strong field for efficient charge generation, separation with minimum recombination

Optical modulation

- Wide band gap, low absorption coefficient, or scattering centers from surface textures

Resistance

- Conductive, easy ion migration and bubble release; facile charge transfer with minimum barrier at C/E interface

Stability

- Chemically inert in interested environment and under interested bias, compact/defect-free, and strong bonding to substrate

A”ctivity

- High catalytic activity, selectivity, large number of surface reaction sites

General design guidelines (“BORSA”) for heterogeneous coatings to enable Si for solar-fuel conversion.

Chem. Rev., 2014

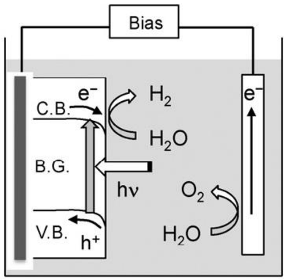
Development of solar-to-hydrogen conversion platform: Silicon photocathode

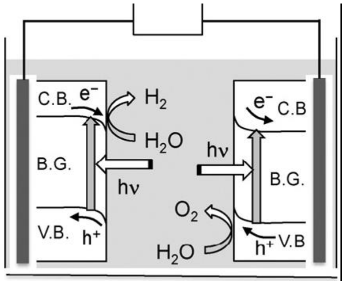
Silicon

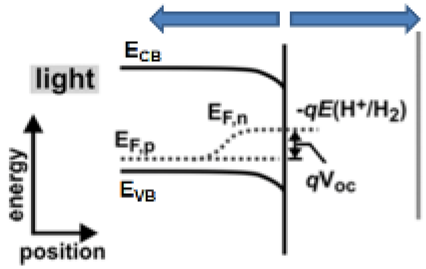
- ✓ Earth abundant and low cost material
- ✓ Low bandgap (1.12 eV) absorbing a significant part of the solar spectrum

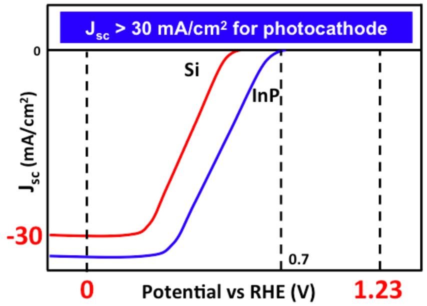
Silicon photocathode

- ✓ Higher conduction band than H^+/H_2 redox potential when interfaced with water
- ✓ Theoretical maximum of single junction Si: limiting current density(~33 mA/cm^2) and photovoltage(~0.5 V)
- ✓ Very low solar-to-hydrogen conversion efficiency due to kinetic barrier for proton transport and the formation of oxidation layer in aqueous solution





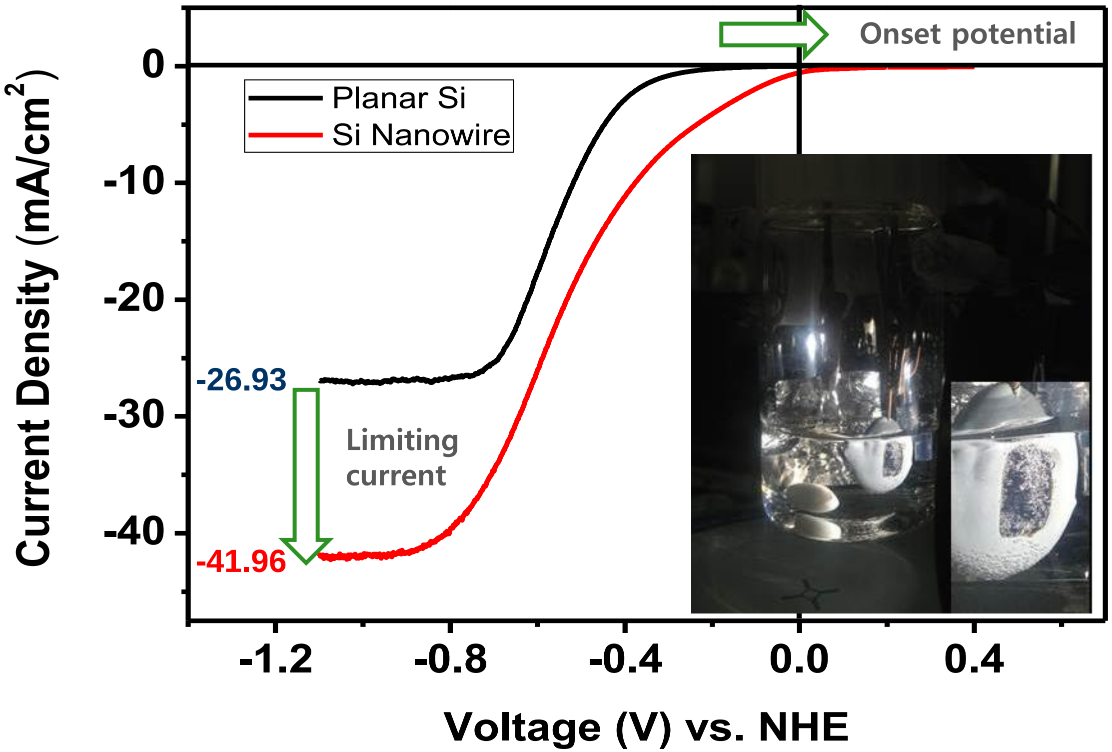




Condition of photocurrent measurement

- ✓ Light intensity of 100 mW/cm^2 and AM 1.5G solar spectrum using 300W Xe lamp
- ✓ 1 M $HClO_4$ (pH 0)
- ✓ 3 electrode system (working, counter, reference)

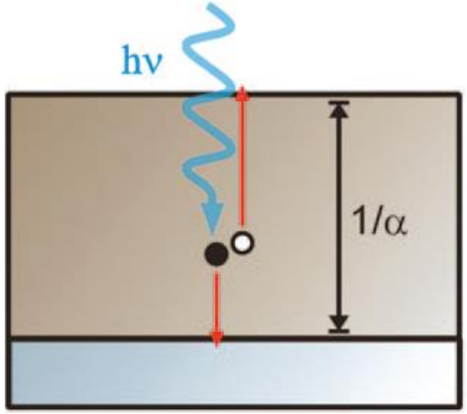
Planar Si and etched Si wire



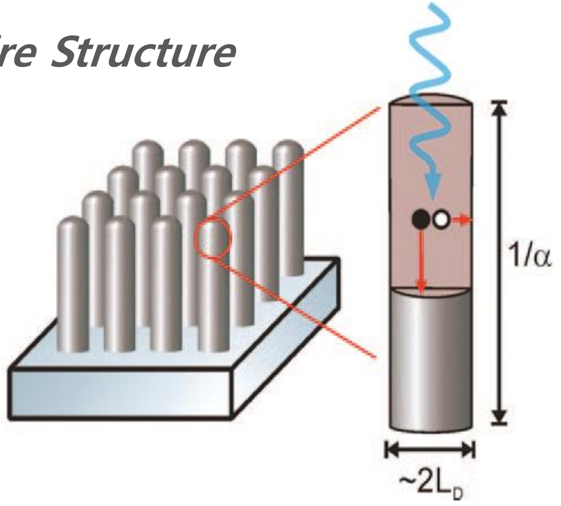
Advantage of Wire Structure

- **Enhanced effective area**
- **Reduced reflection**
- **Orthogonalization of light absorption and charge-carrier collection**

Planar Structure

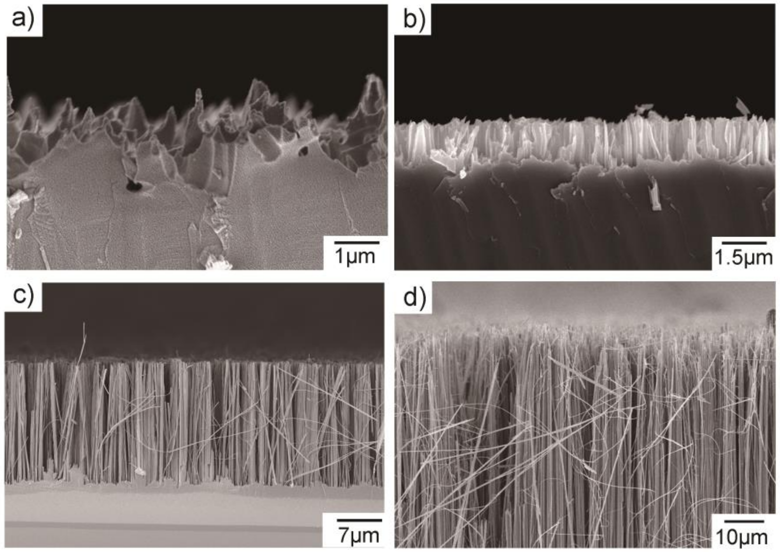


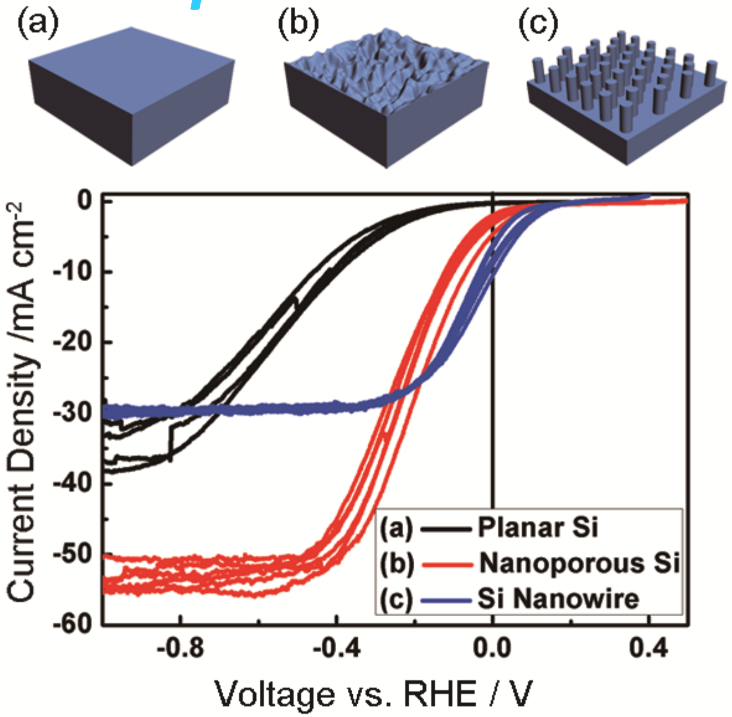
Wire Structure



L_D :the diffusion length
α: the absorption coefficient of the semiconductor near the band gap energy.
1/α: optical thickness

Nanostructural dependence on Si photocathode



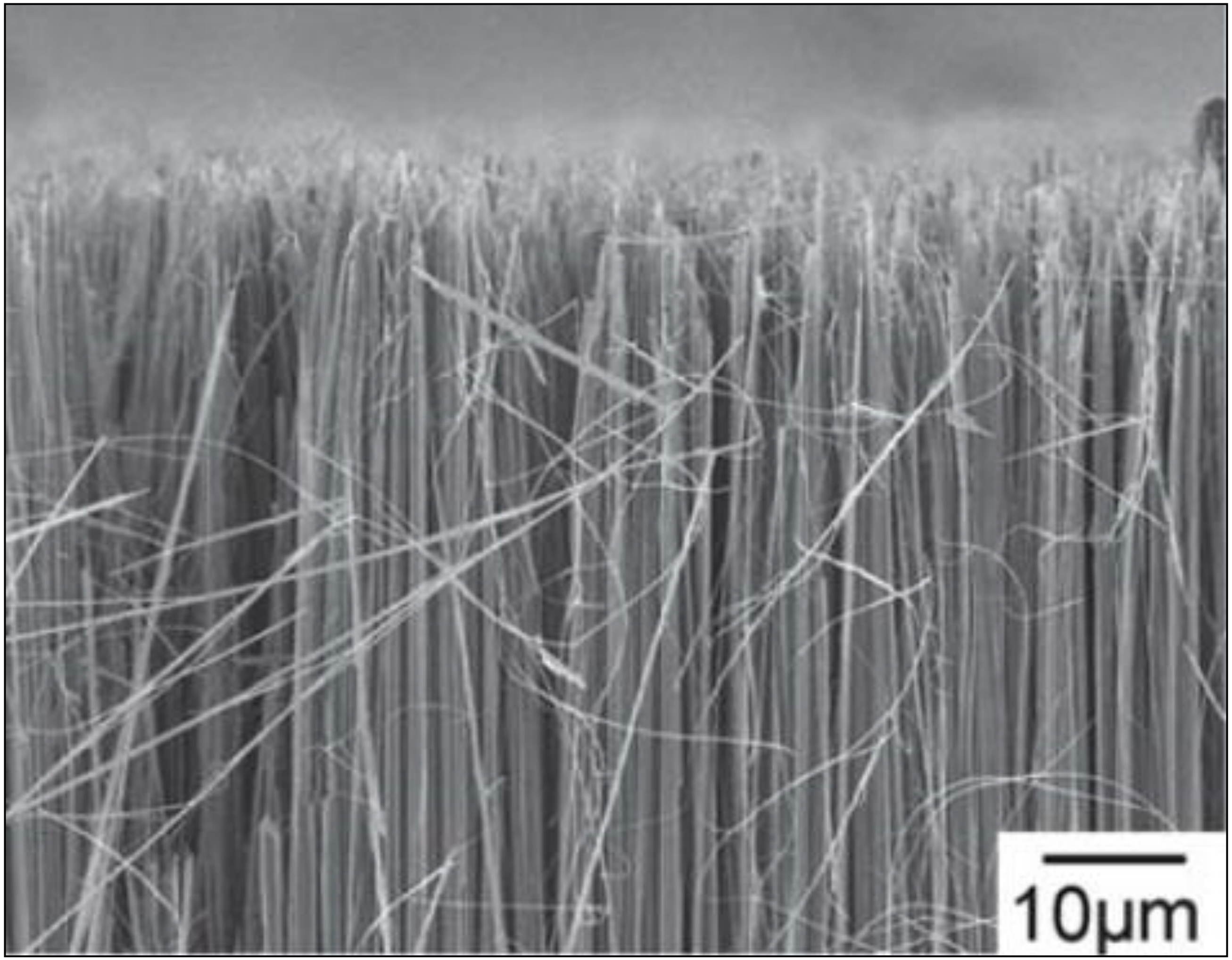


Silicon nanowire was fabricated by **Metal-Catalyzed Electroless Method**

The optimum nanostructure of a Si photocathode exhibits an enhanced photocurrent and a lower overpotential compared to the planar bulk Si.

The solar-to-hydrogen conversion efficiency of the optimized Si nanowire without depositing any catalyst has reached up to about **70% of the efficiency of planar Si decorated with Pt.**

Si Nanowire Photocathode



Planar Si

Nanostructured Si

Diffusion length $L_D = \sqrt{D\tau} \geq {}^{1}/_{\alpha}$

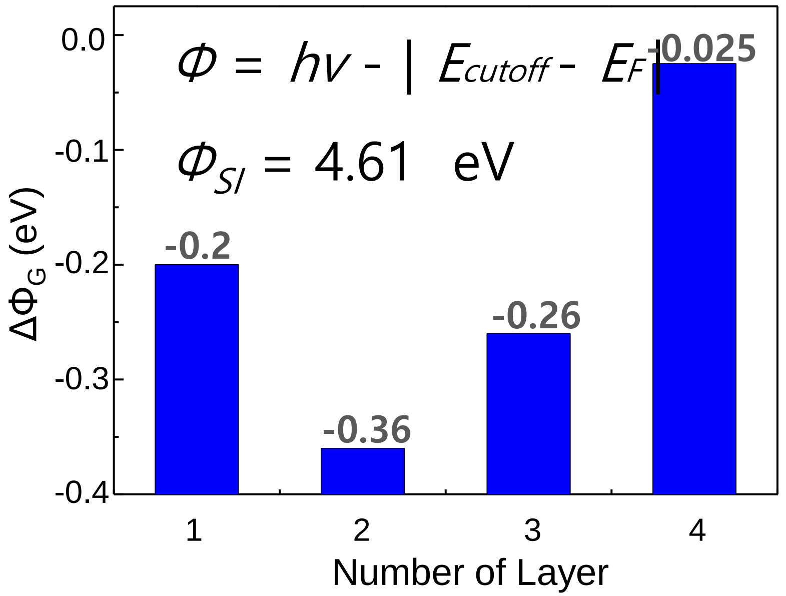
Onset potential $V_{os} = \frac{kT}{q} \ln \frac{J_{ph}}{\gamma J_o}$

Efficiency: 1.19% (43 times higher than bare Si)

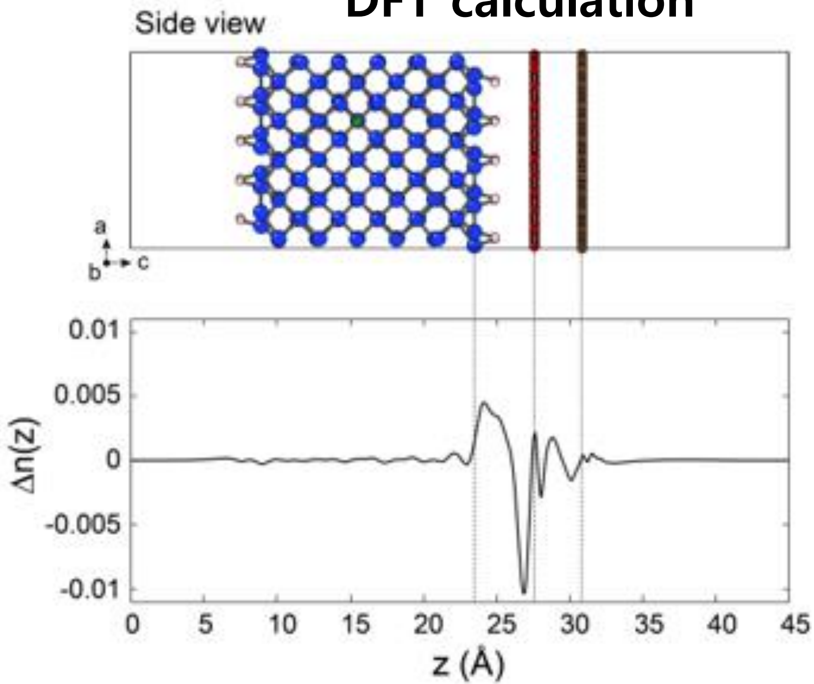
Uk Sim et al., J. Mater. Chem. A. (2013)

Mechanism at the interface

UPS measurement



DFT calculation

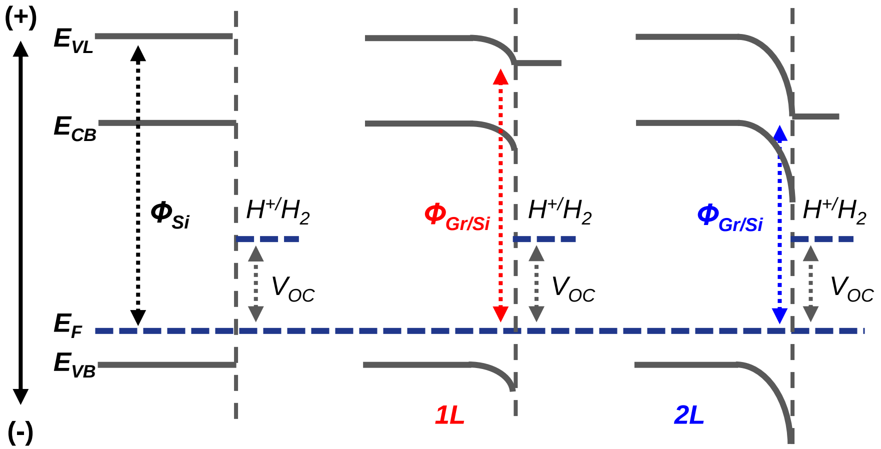


Increased density of states

→ Further Coulombic shift

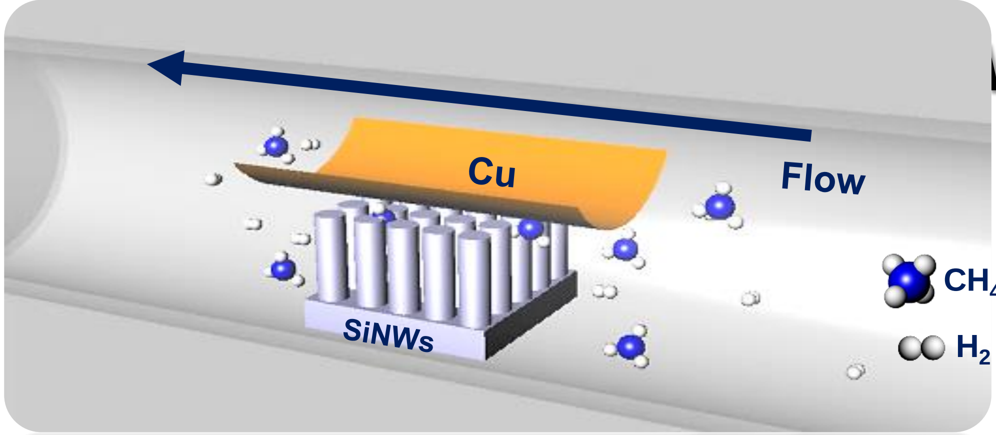
→ The smallest work function

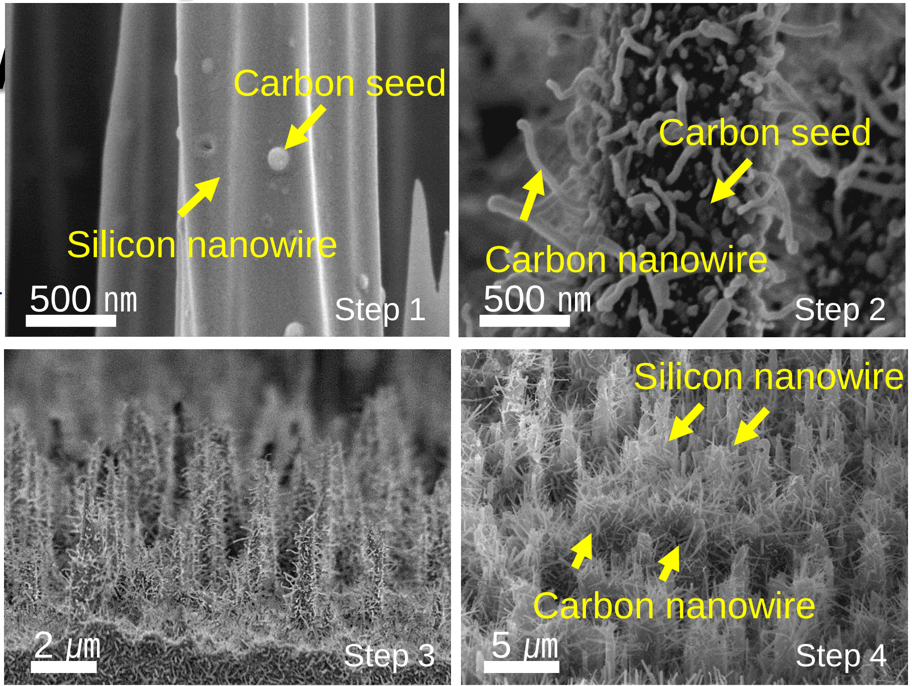
→ The highest band bend bending

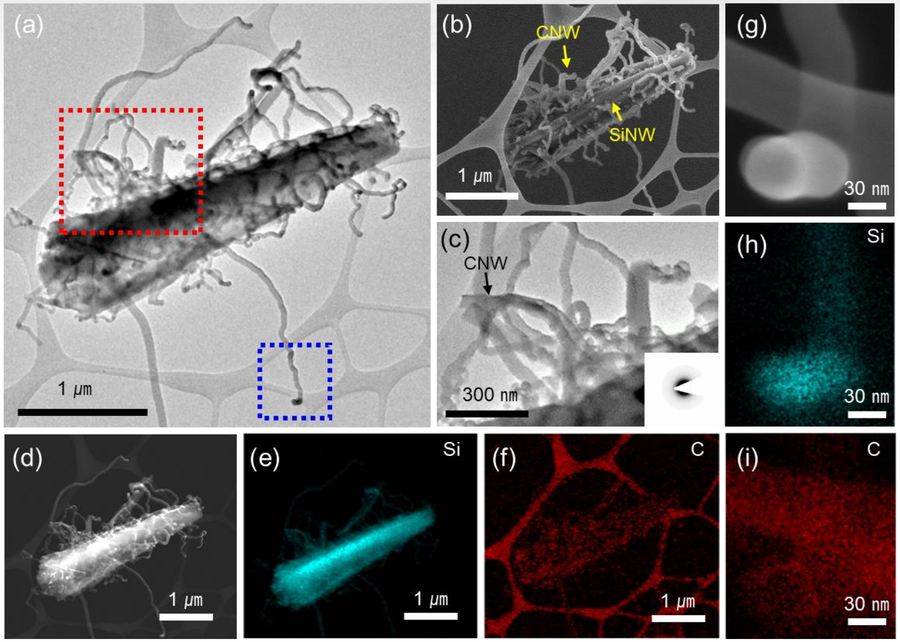


Importance of the electronic band structures of catalytic surface on photoelectrode

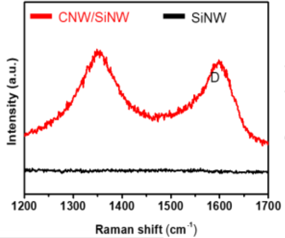
Hierarchical branching carbon nanowire catalyzed by copper-vapor on silicon

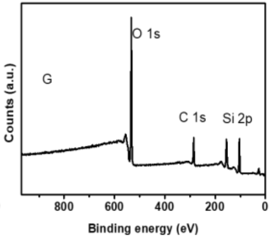


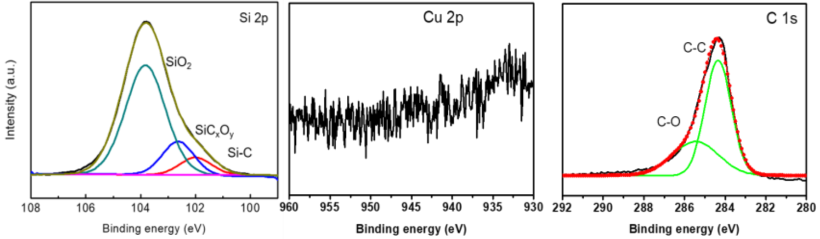




TEM and SEM images of CNW grown on SiNW by using Cu vapor.



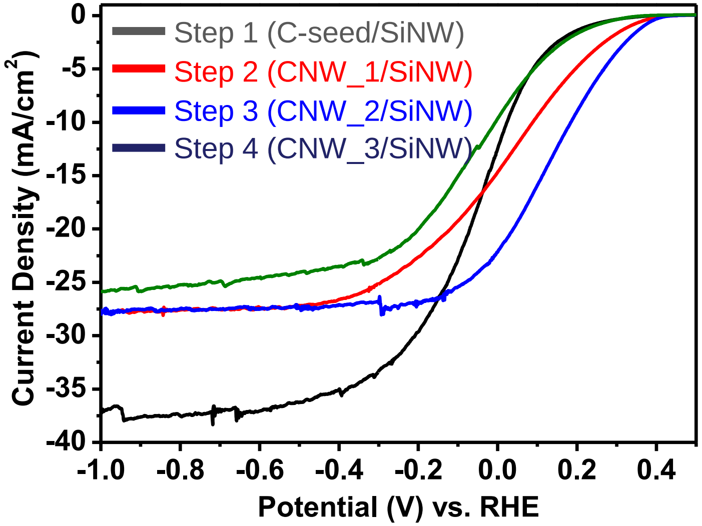


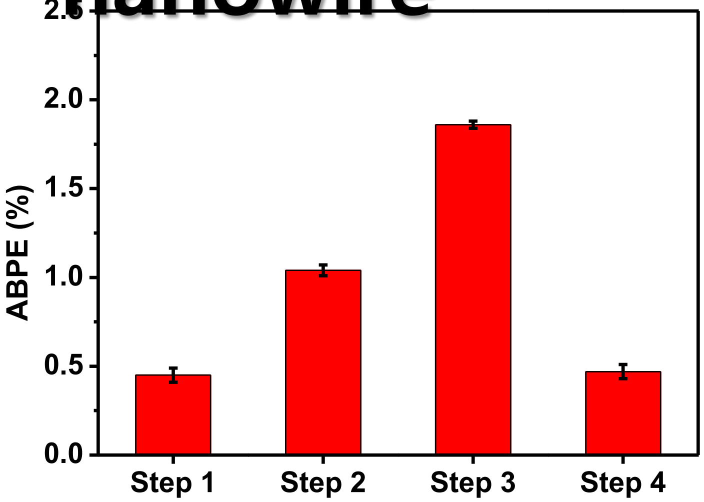


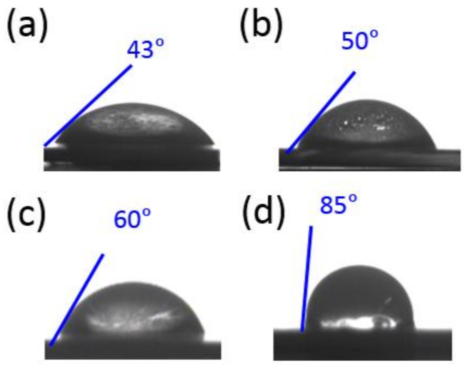
Uk Sim et al., Nanoscale (2018)

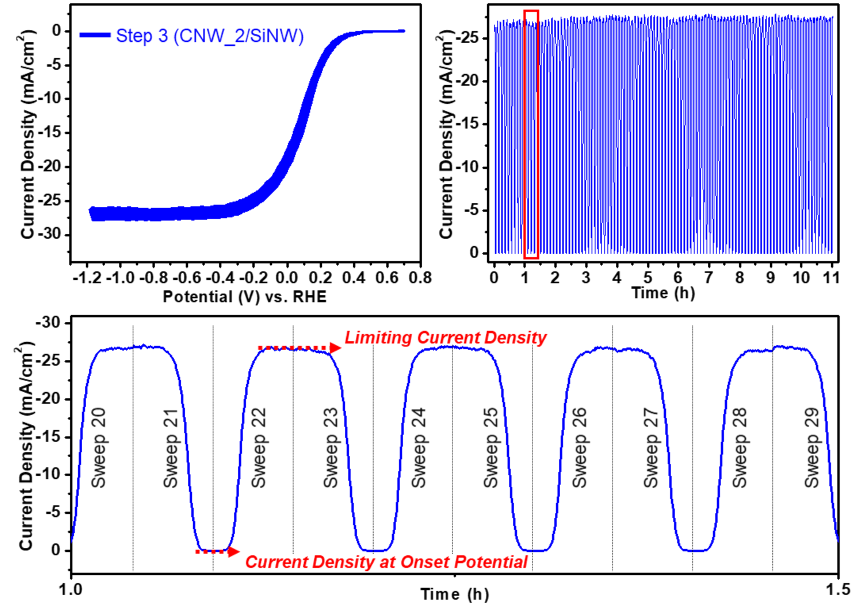
Hierarchical branching carbon nanowire catalyzed by copper-vapor on silicon nanowire

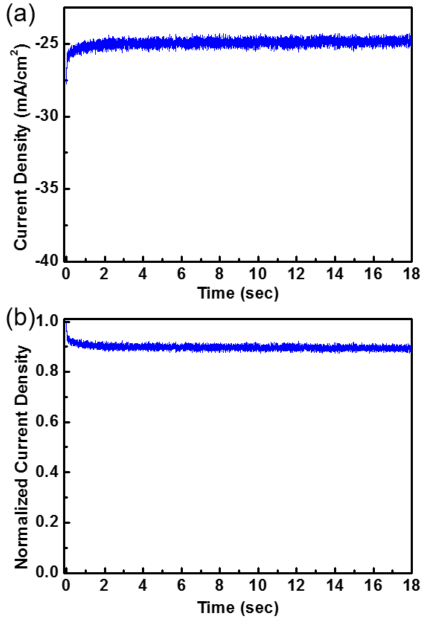
Uk Sim et al., Nanoscale (2018)

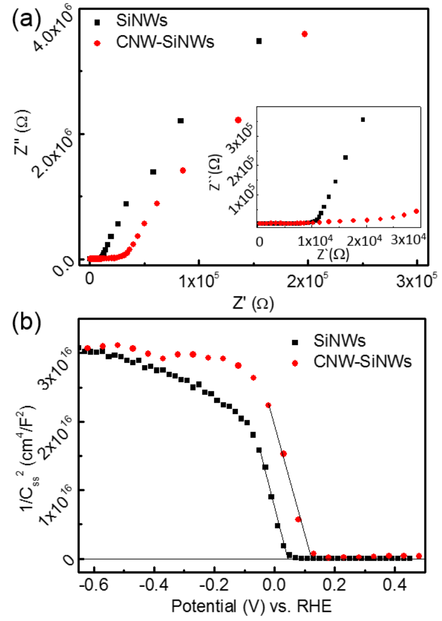






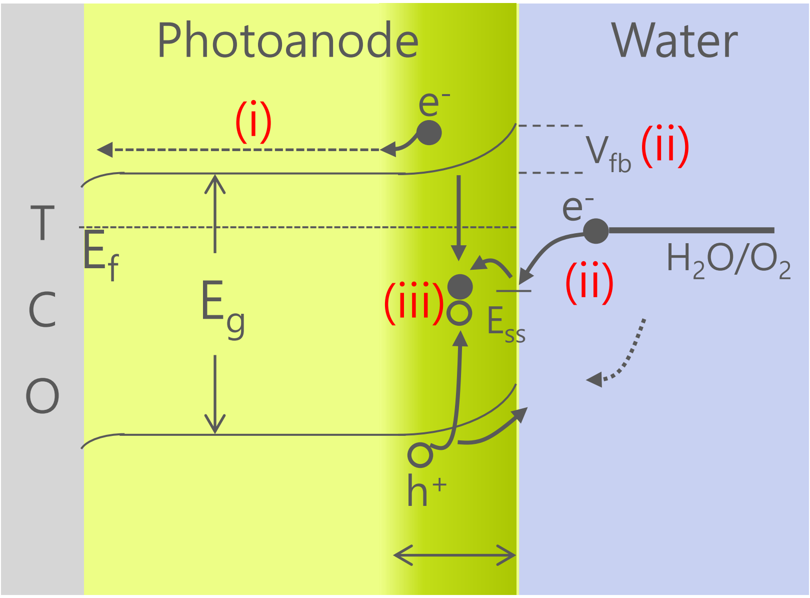


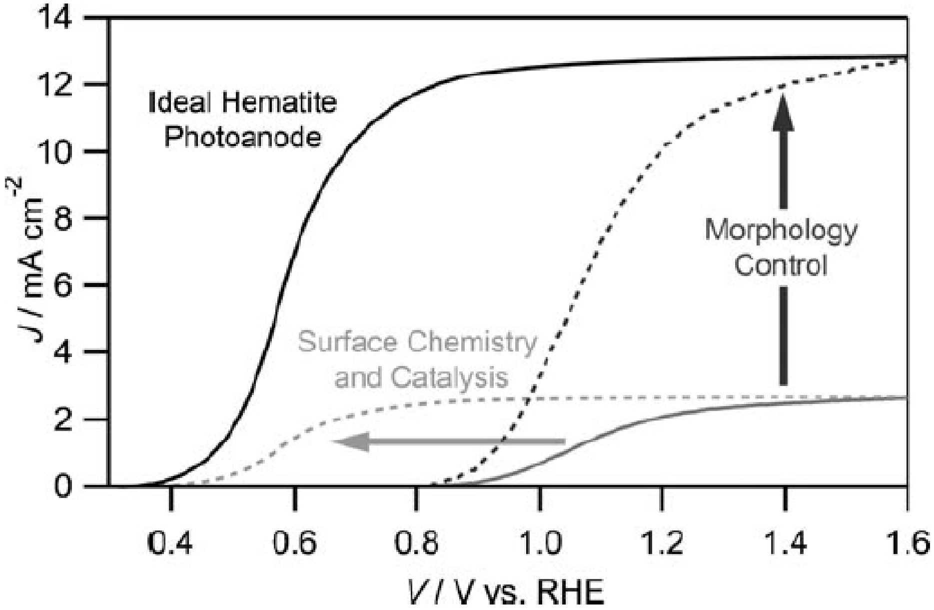




Strategy of research for design of photoanode

- Poor majority carrier conductivity (i)
  → high-level **doping**
- Too low flat band potential
  → external bias / band tuning
- Overpotential: surface trap or poor OER (ii)
  → surface treatment / **catalysis**
- Saturartion current: Short diffusion length of minority carriers (hole) (iii)
  → morphology control / **nanostructure**





K. Sivula *et al.*, *ChemSusChem* **4**, 432 (2011)

Hematite (α-Fe_2O_3) Photoanode

The most common form of iron oxide.

- Fe: 4th abundant element in the earth's crust
- O: 21 % of the air

Low cost
nontoxicity

Iron is readily oxidized in the presence of water. "Rust"

- Hematite is very stable in aqueous solution.

Chemical
Stability

The ability to absorb light.

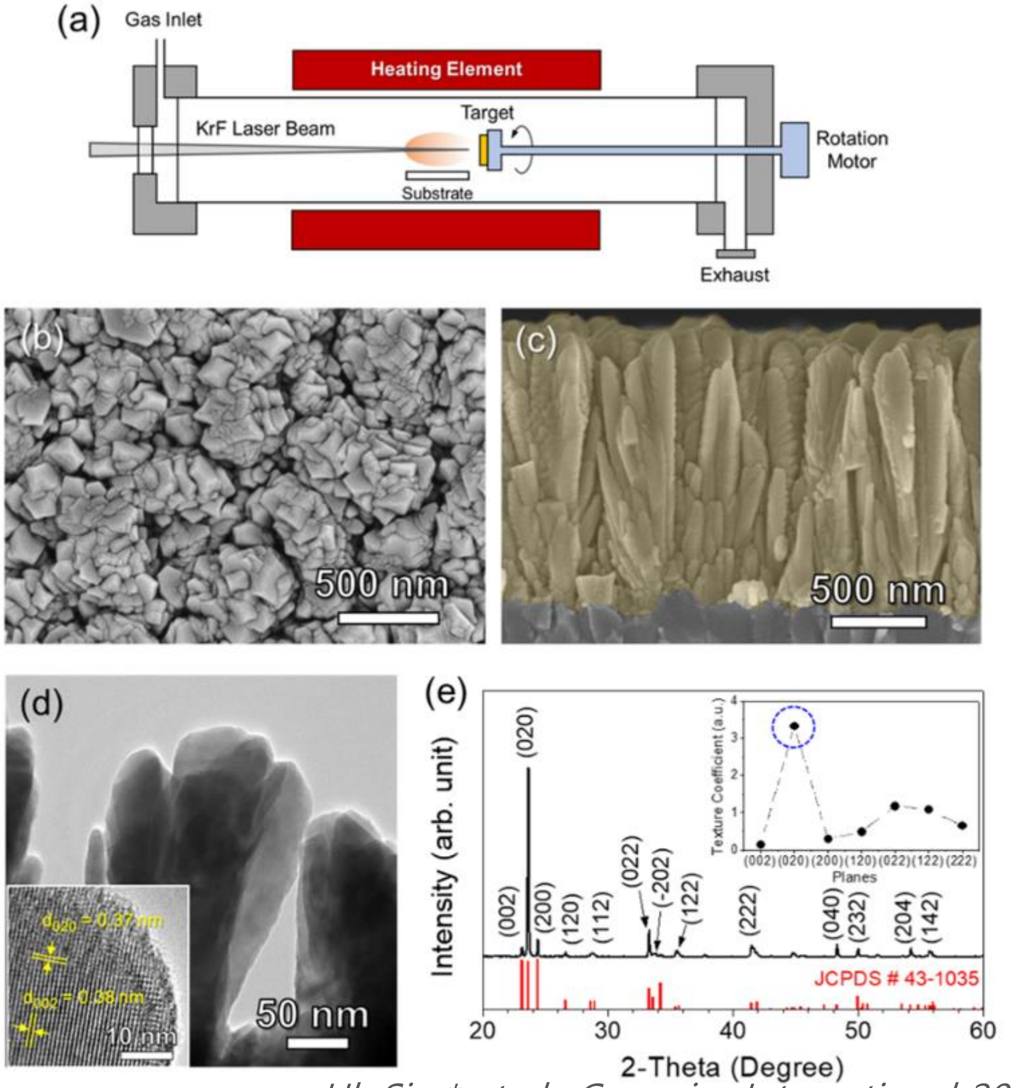
- Hematite is used as pigments in paints and even cosmetics.

Visible-light
absorption

Hematite is an attractive material for use in solar water oxidation.

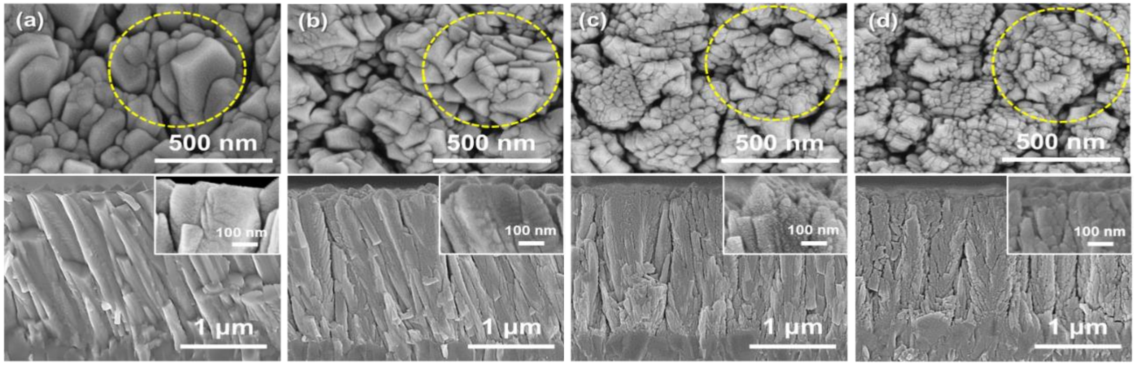
(020)-Textured WO_3 via laser ablation method

Metal oxides (ex. TiO_2, Fe_2O_3, $BiVO_4$, WO_3) have been promising candidates for the photoanode

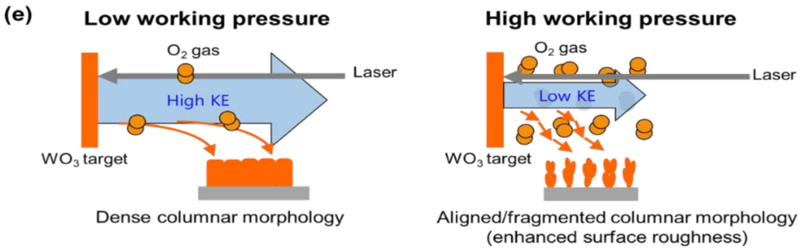


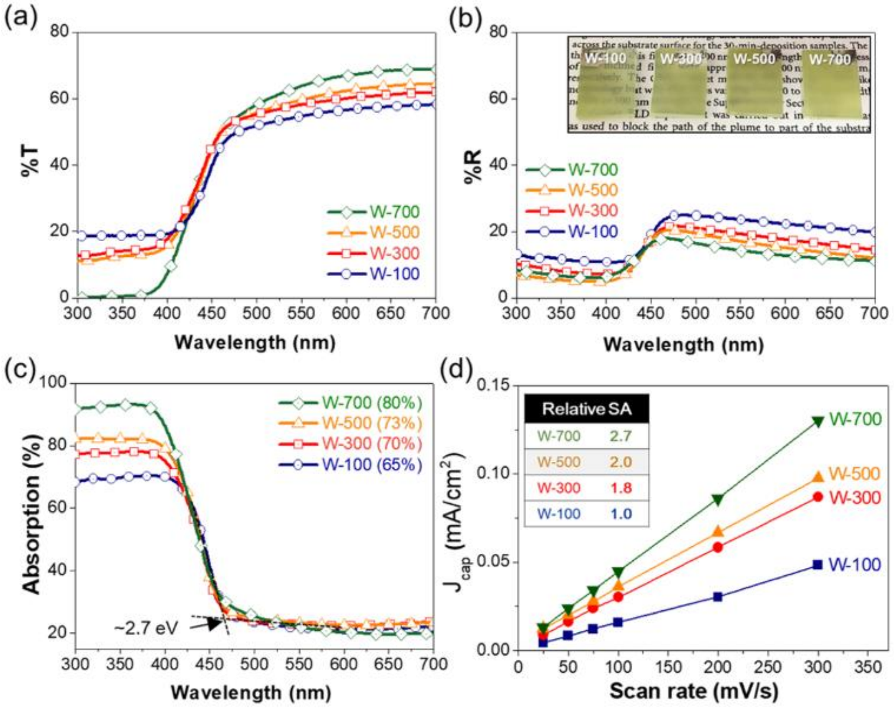
Uk Sim et al., Ceramics International 2021, 47 (3), 3972-3977*

WO_3 via Texture and Nanostructure Control



- Morphology and thickness control through oxygen partial pressure (100~700 mTorr)
- Schematics (e) shows how the partial pressure effects the morphology.

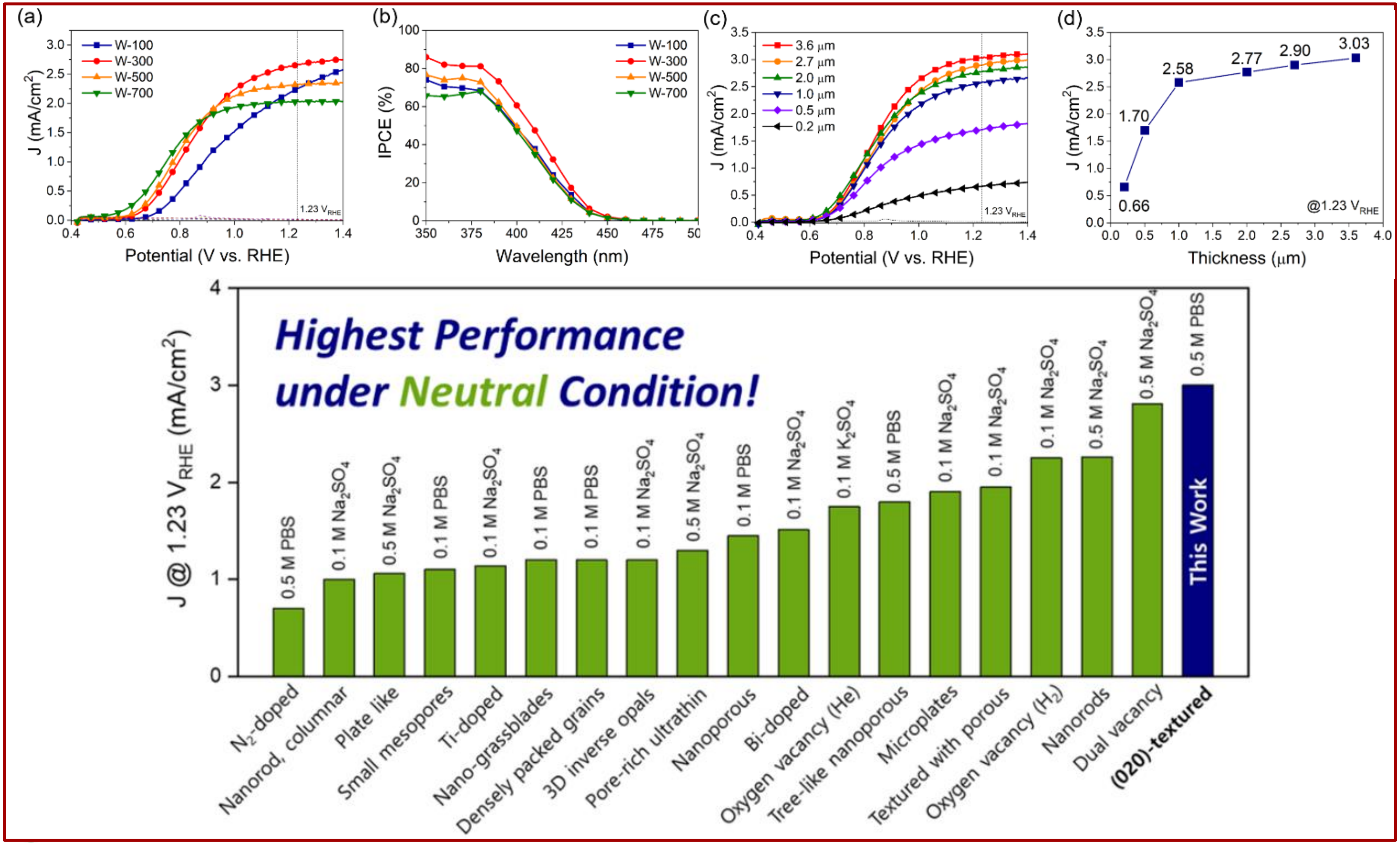




Relative SA	
W-700	2.7
W-500	2.0
W-300	1.8
W-100	1.0

- Optic properties were investigated through absorption, transmittance, reflectance measurement.

WO_3 via Texture and Nanostructure Control



Morphology Control of TiO_2 Nanorods Photoanode