Photoelectrochemical water splitting system for biocatalytic hydrogen production

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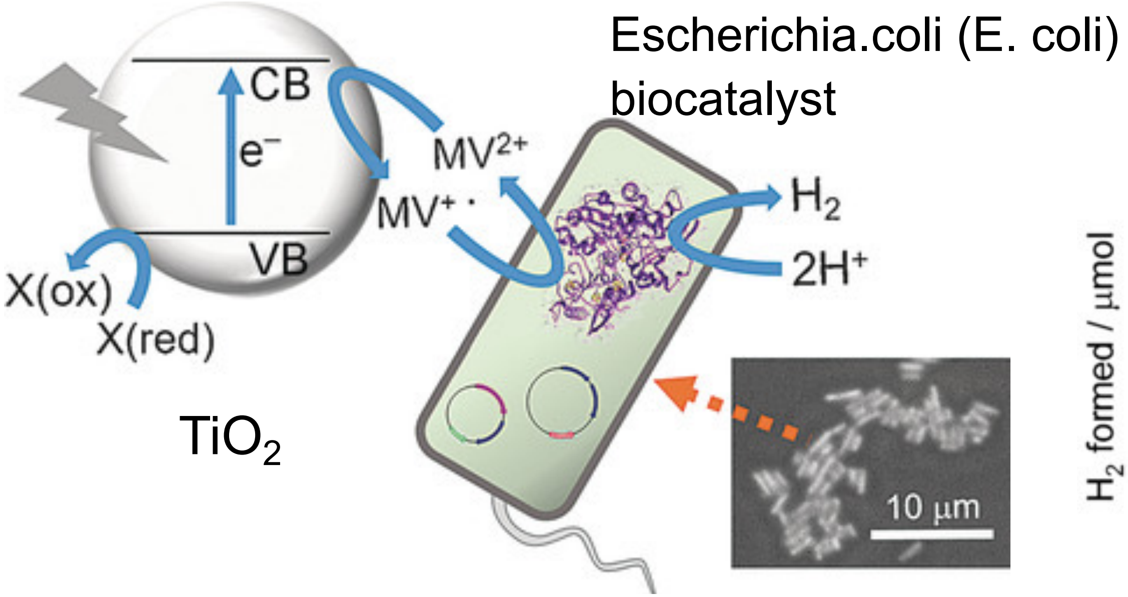
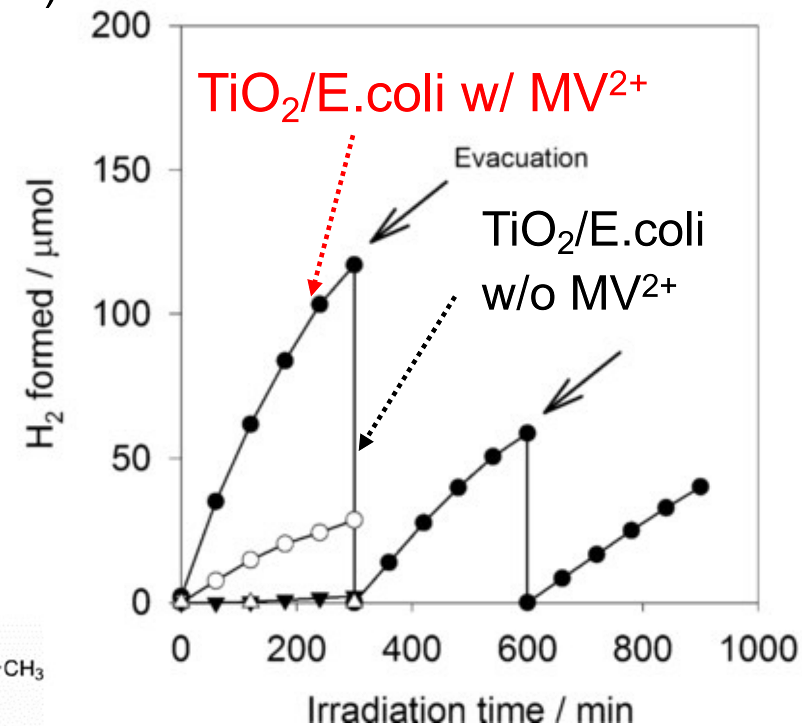
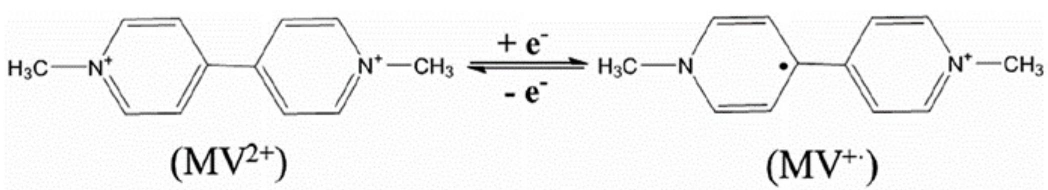
Inorganic-bio hybrid photocatalytic H_2 production





w/ 300 W Xe lamp

Redox mediator: methyl viologen (MV)



- E.coli cell: H_2-forming site in inorganic-bio hybrid photocatalytic system
- Redox mediator (MV) boosts hydrogen evolution

→ **Redox mediator should be key factor for biocatalytic H_2 production !**

Honda et al., *Angew. Chem.* 2016, 128, 8177

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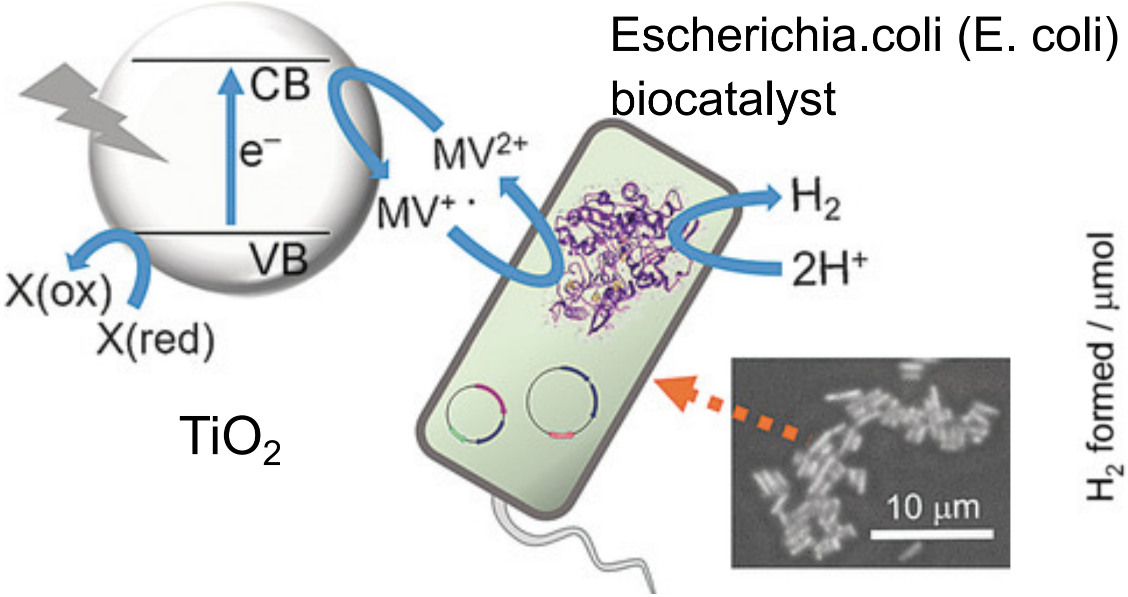

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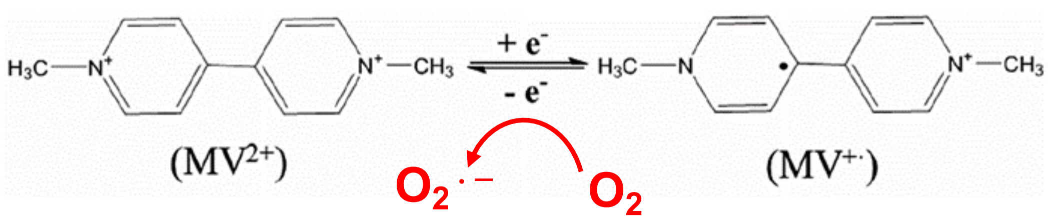

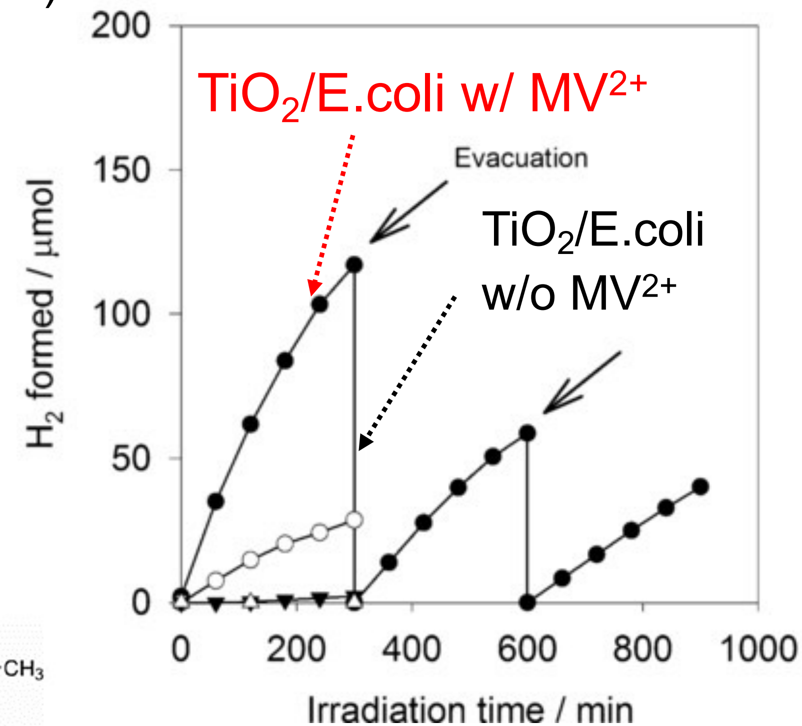

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Reversible reaction of MV^+ by oxygen → Obstacle for overall water splitting

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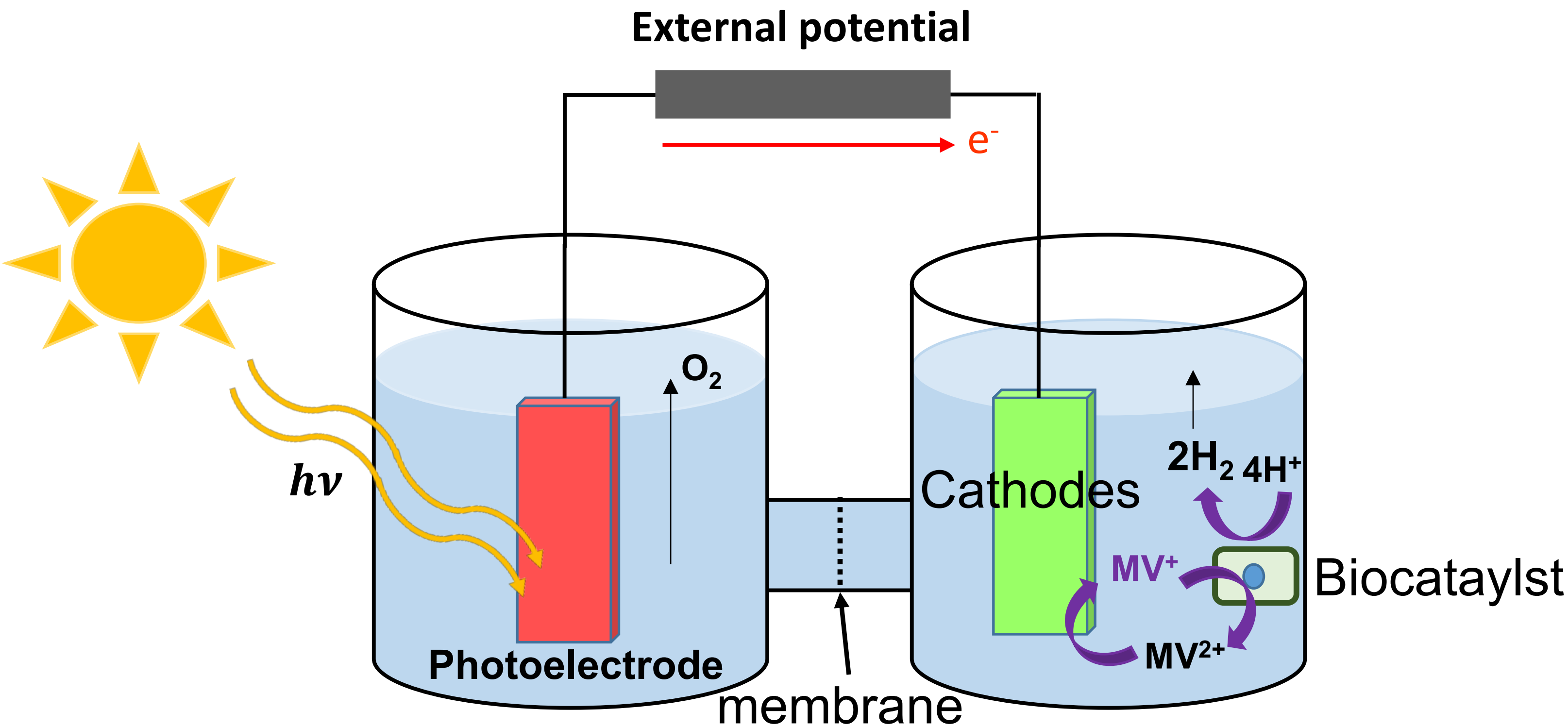
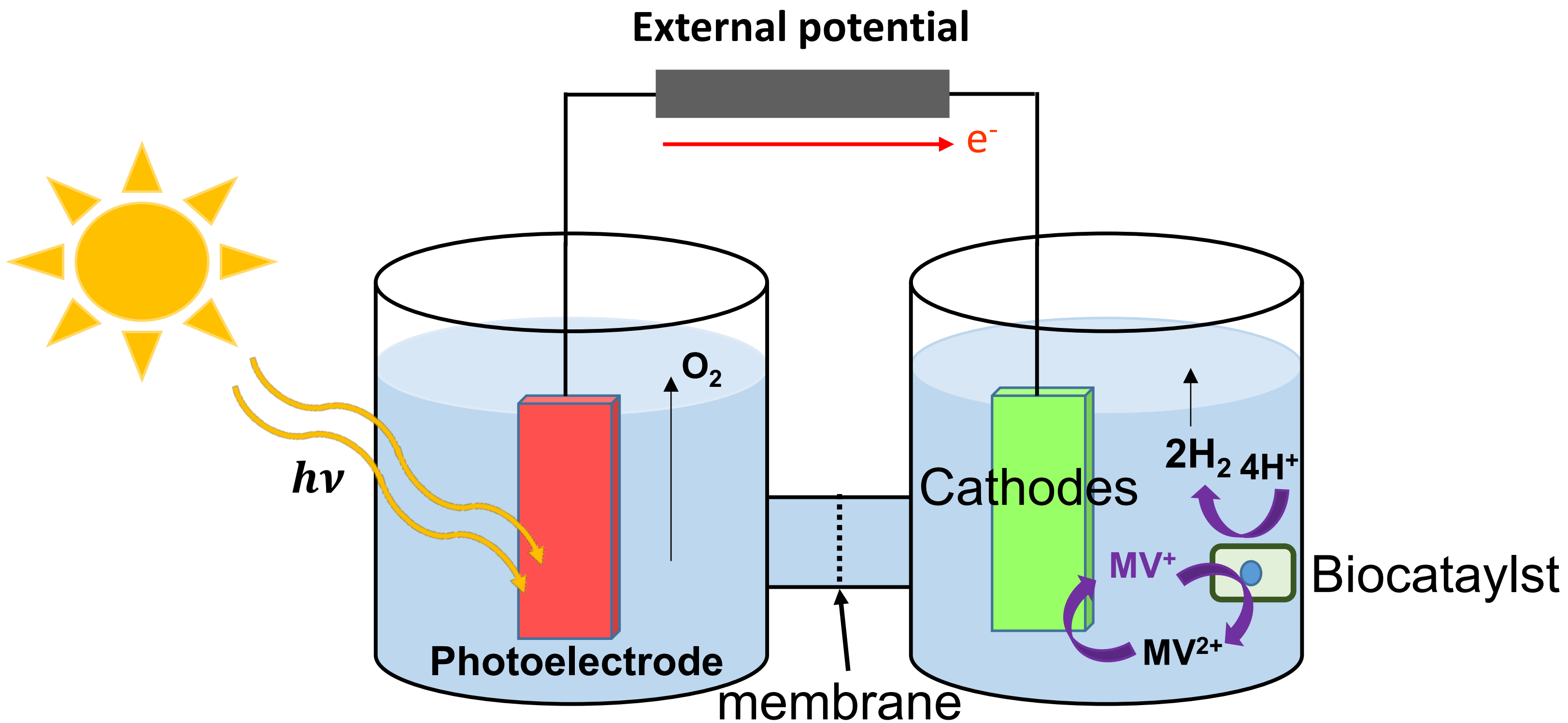
Photoelectrochemical (PEC) system approach



PEC configuration separates H_2 & O_2 evolution sites

:: Enables overall water splitting

Photoelectrochemical (PEC) system approach



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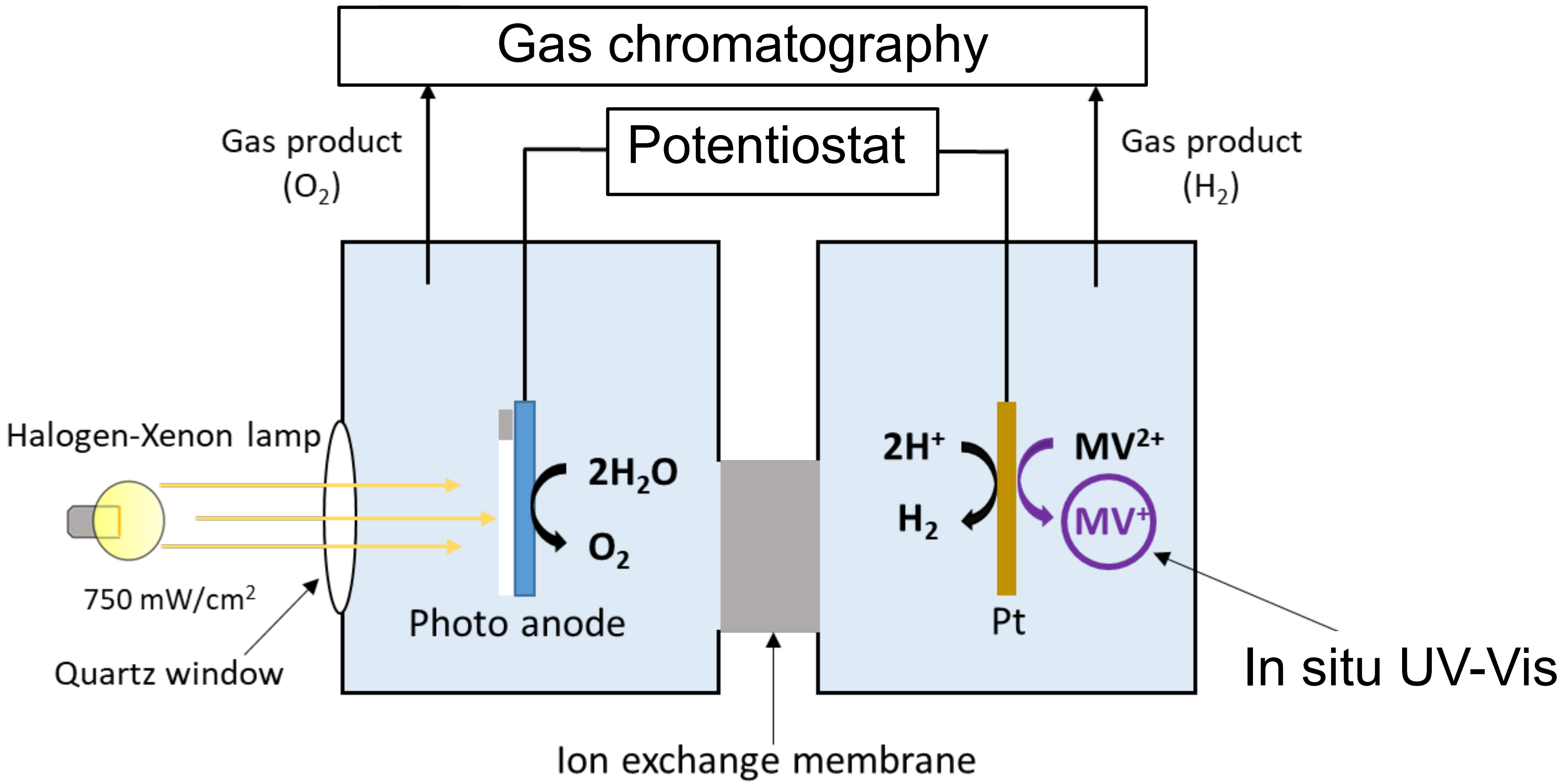
Research issues & purpose

1. The behavior of electrochemical reduction of MV^{2+}
   - Investigation of cathode materials
2. Light-driven PEC cell's operation
   - PEC demonstration with TiO_2 model electrode

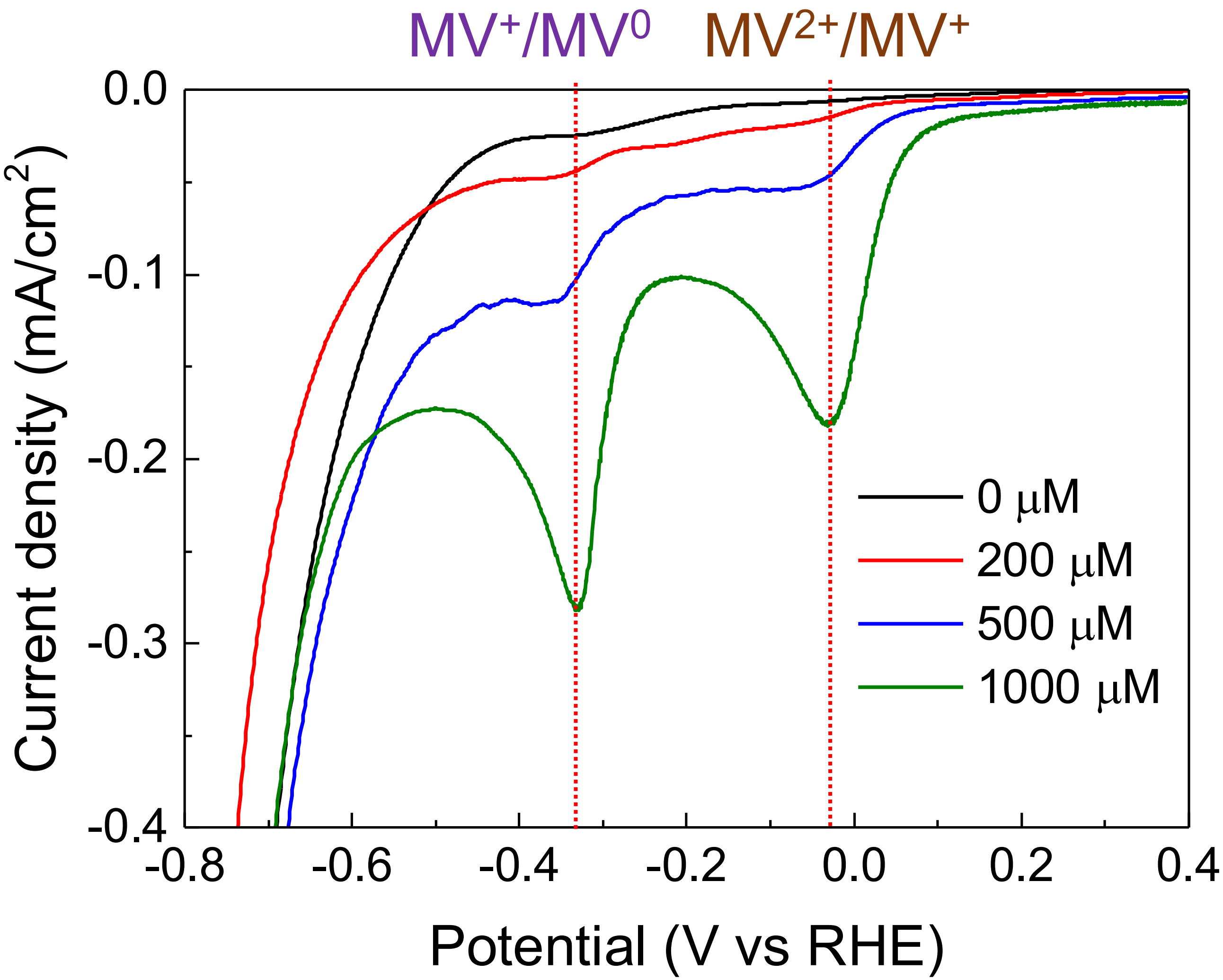
Experimental Method



(Photo)Electrochemical evaluation condition (three-electrode configuration)

- Working electrode (WE) :
  - Cathode materials: Au, Ag, Pt, Ni,
  - Anode: TiO_2 (coated on FTO by electrophoresis method)
- Counter electrode (CE) : Pt wire
- Reference electrode (RE) : Ag/AgCl in 3.0M NaCl
- Electrolyte: 1.0M KOH +1.0M KH_2PO_4 (pH=8) + MV

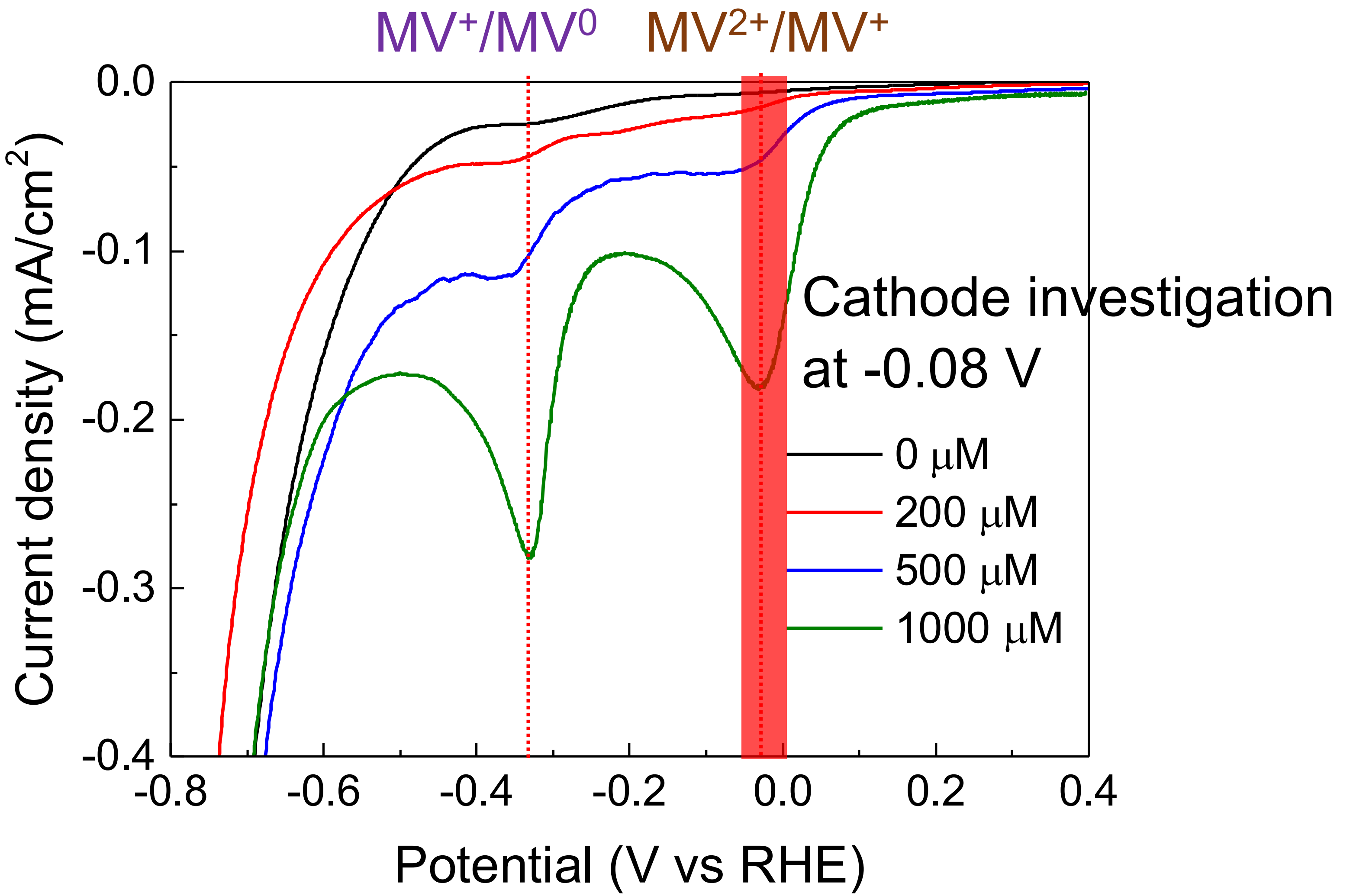
Electrochemical behavior of MV



MV concentration dependence with Ag cathode

- Reduction potentials for MV^{2+}/MV^{+} & MV^{+}/MV^{0} are -0.08 V & -0.[illegible]3 V.
- Higher concentration of MV increases current density.

Electrochemical behavior of MV



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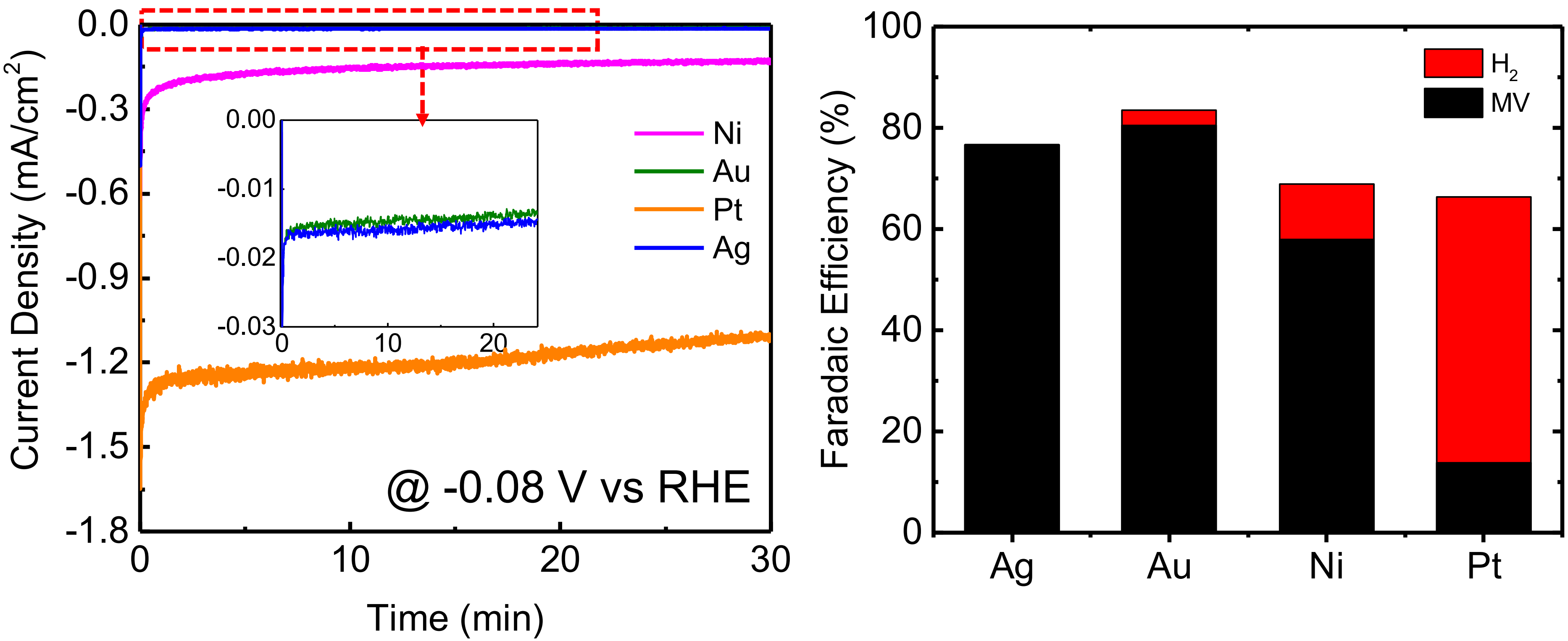
Cathode materials property on MV^{2+} reduction

✓ The effect of cathode material on MV^{2+} reduction



- Ag, Au, Ni: High Faradaic efficiency for MV reduction, low current density
- Pt: the highest current density due to superior H_2 evolution activity

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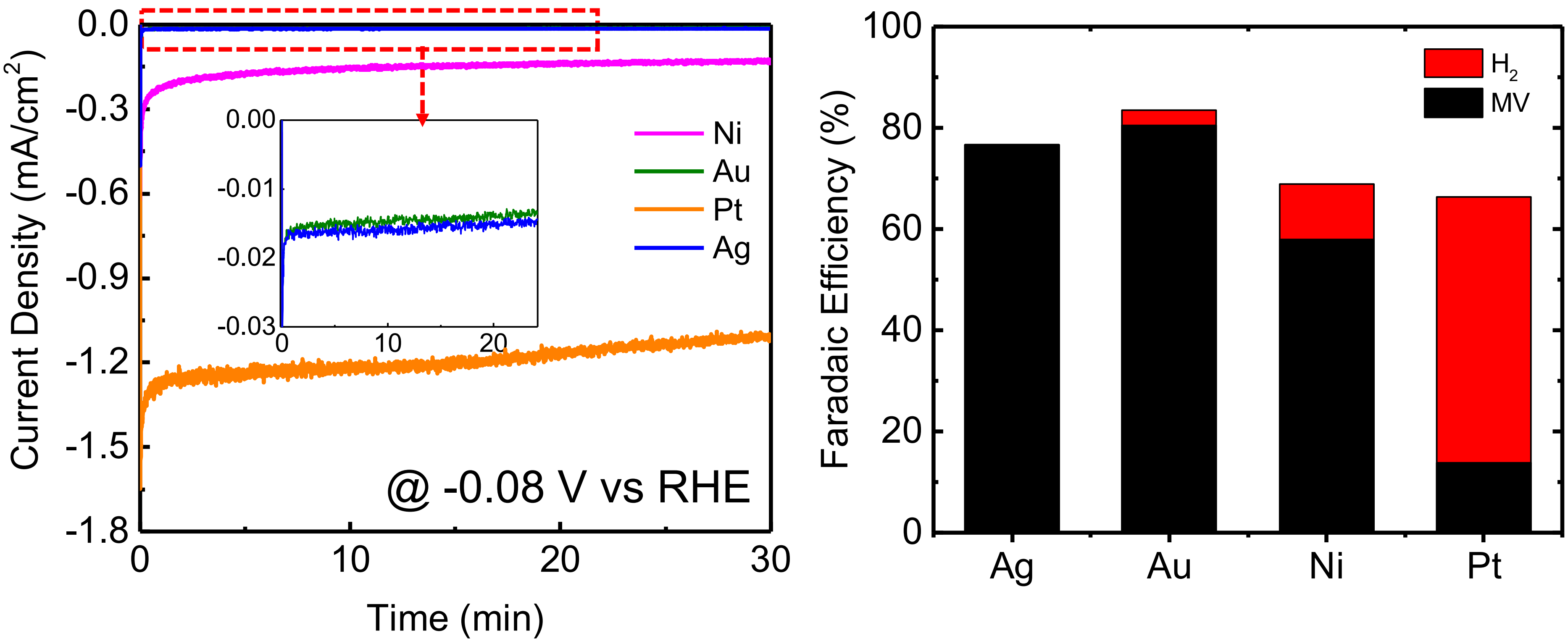

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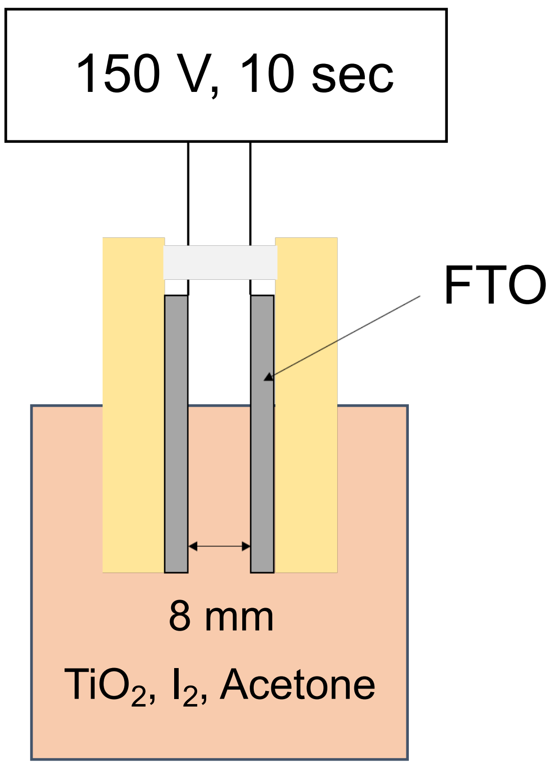
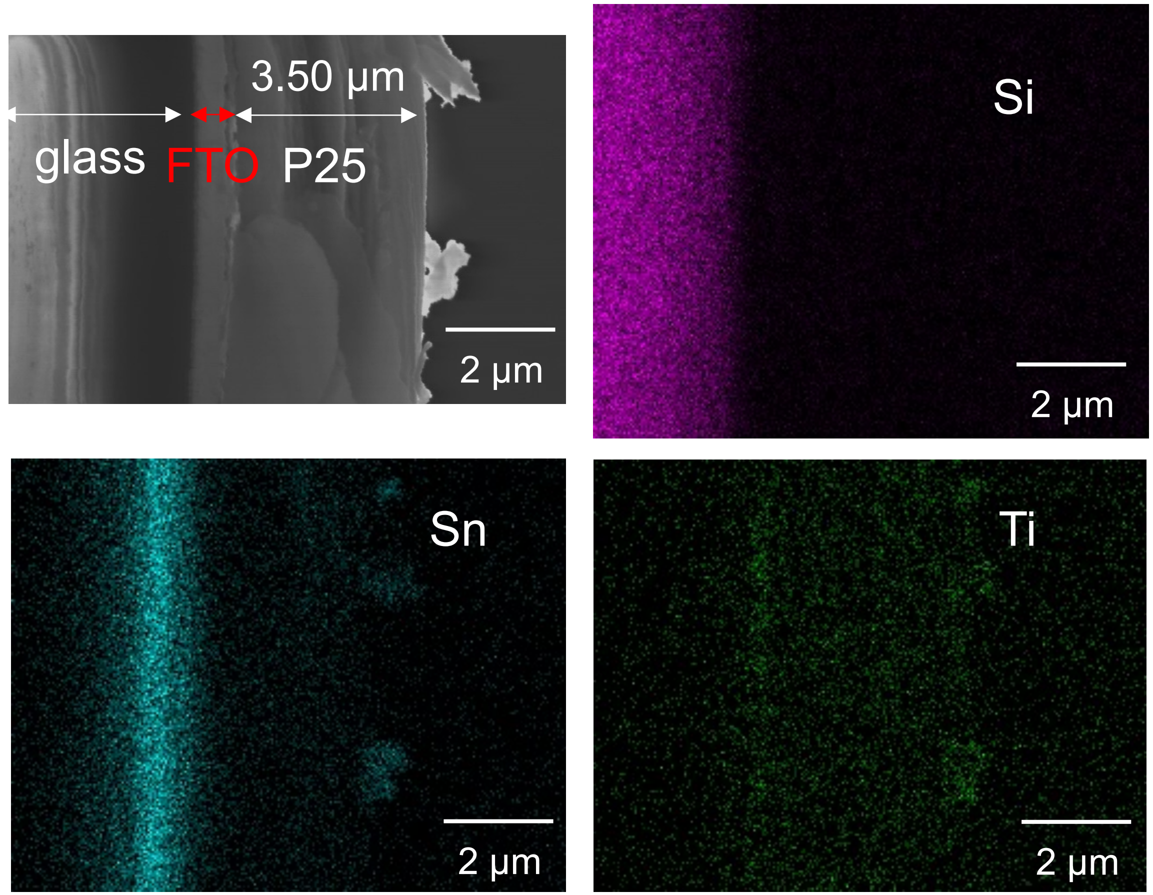
Partial current density: $J_{MV2+/MV+}$ = total current density (J) x Faradaic efficiency

$J_{MV2+/MV+}$ for Pt = 0.17 > $J_{MV2+/MV+}$ for Ni = 0.09

Fabrication of TiO_2 anode



Electrophoretic deposition

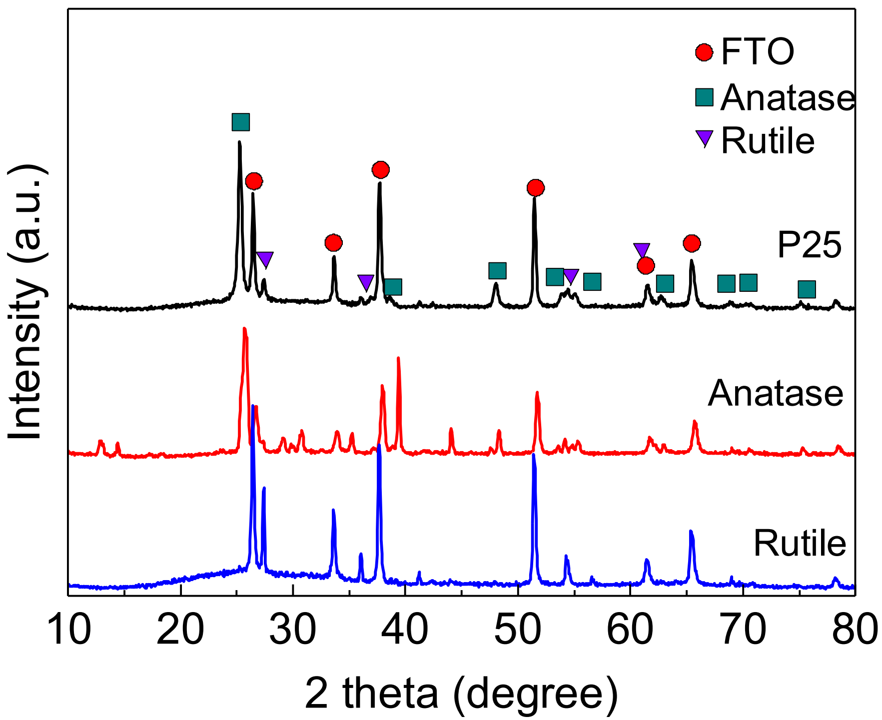


SEM & EDX mapping images of P25 TiO_2 electrode

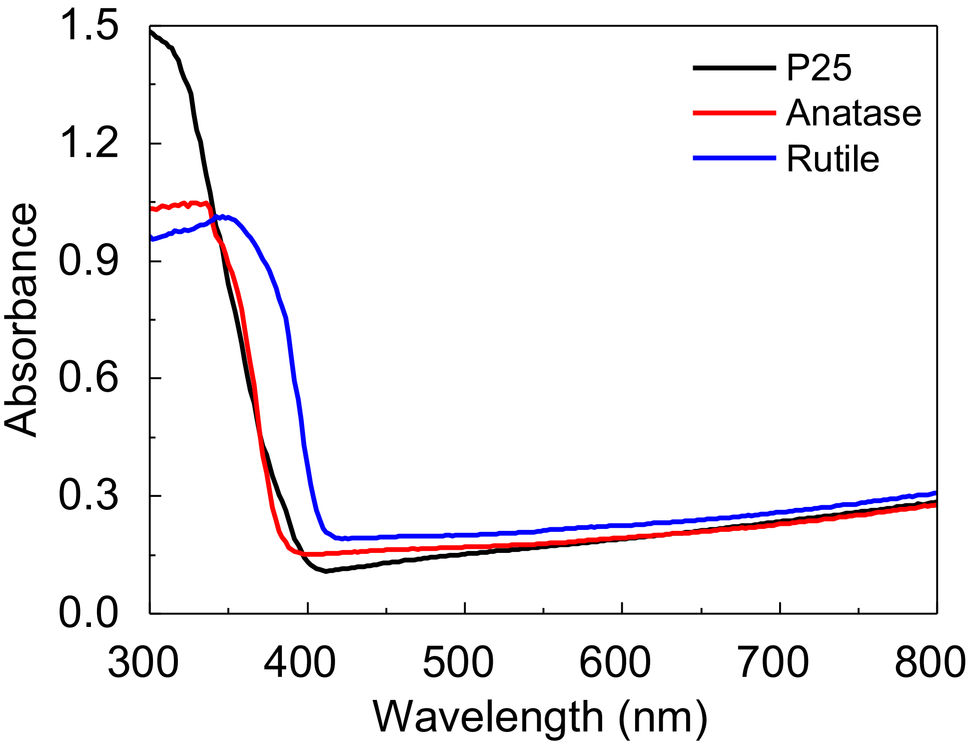
- Via electrophoresis, we prepared ~3.5 μm TiO_2 anode on FTO substrate.

Characteristic of TiO_2 anode

✓ XRD patterns



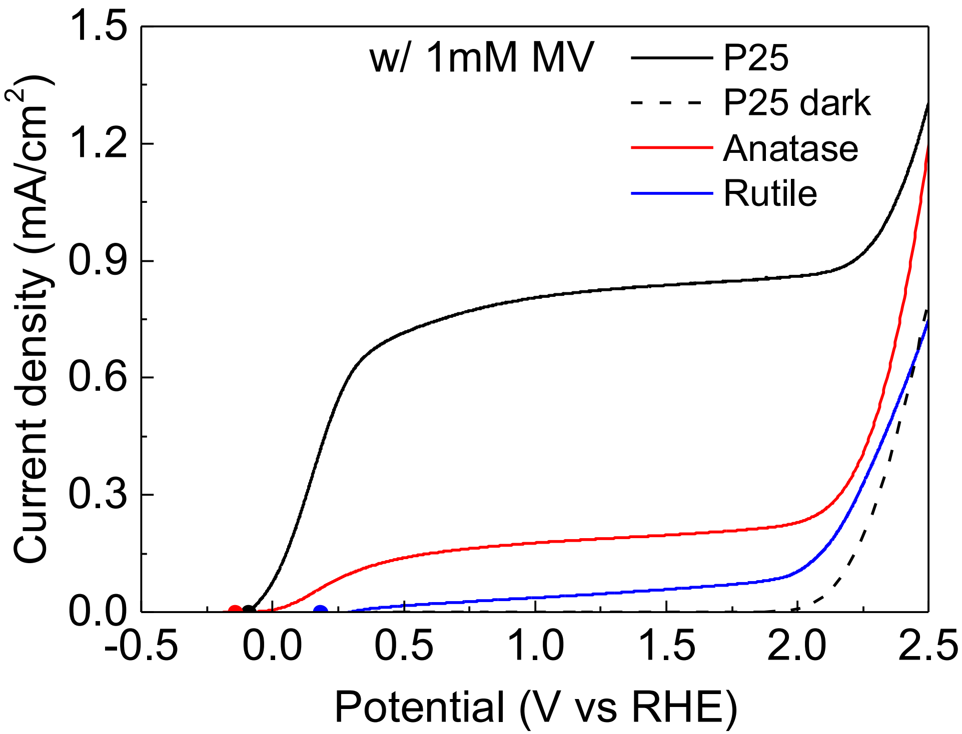
✓ UV-Vis spectra



- P25, anatase and rutile type of TiO_2 are deposited on FTO glasses.
- XRD & UV-Vis confirm each of TiO_2 phases is successfully prepared.

Electrochemical behavior of TiO_2 anode

✓ I-V curves w/ light illumination



- P25 shows the highest PEC activity.

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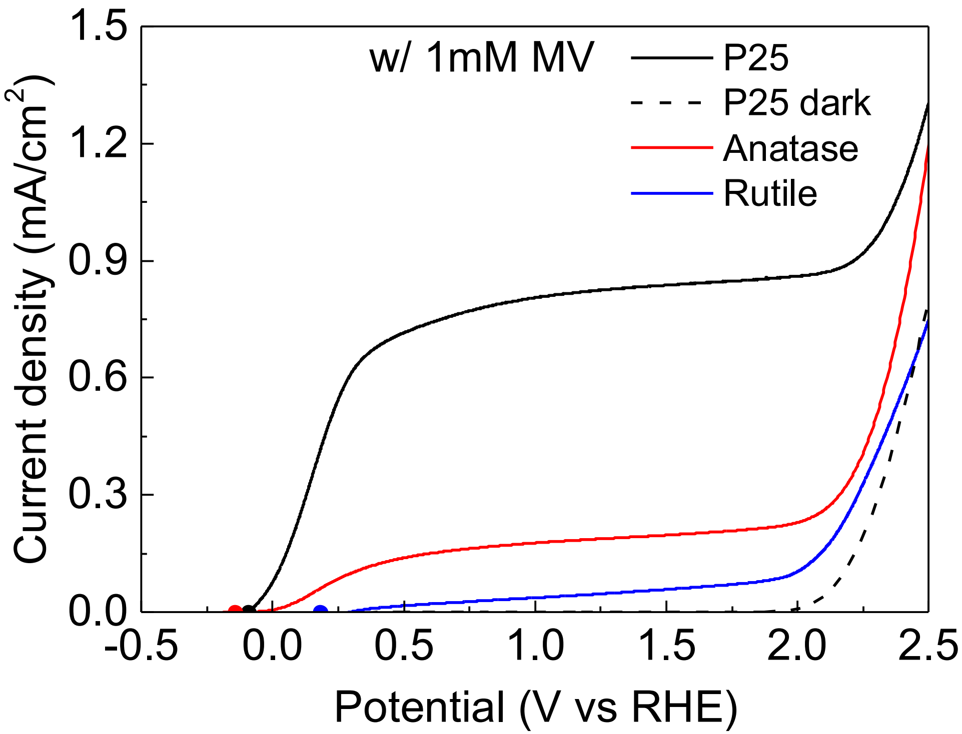
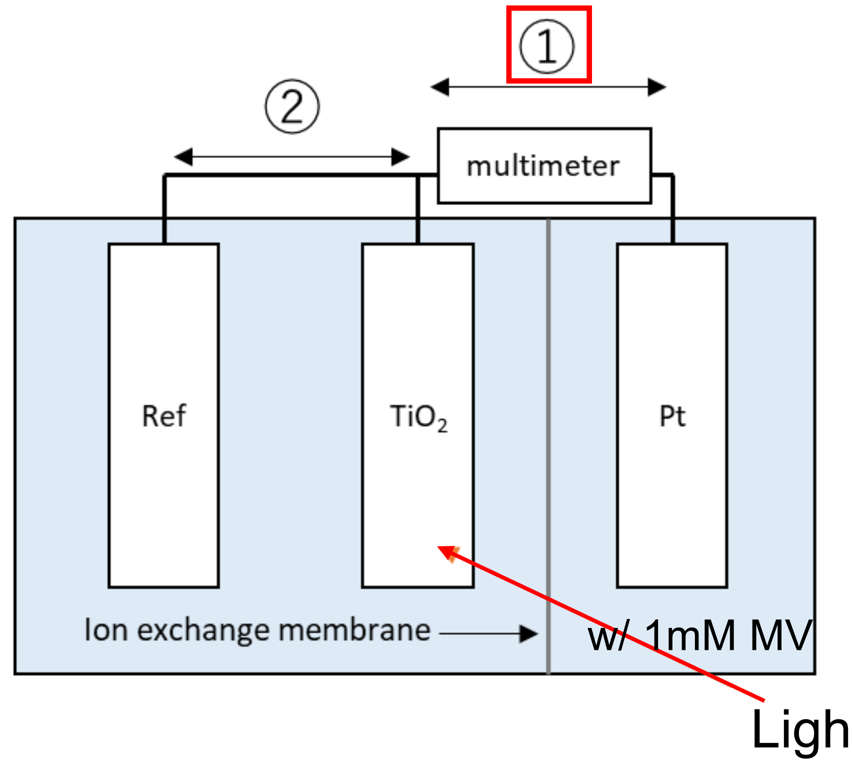


- P25 shows the highest PEC activity.
- Higher photovoltage for P25.

✓ Open-circuit property



	① Open-circuit potential
P-25	-1.08 V
Anatase	-1.07 V
Rutile	-0.82 V

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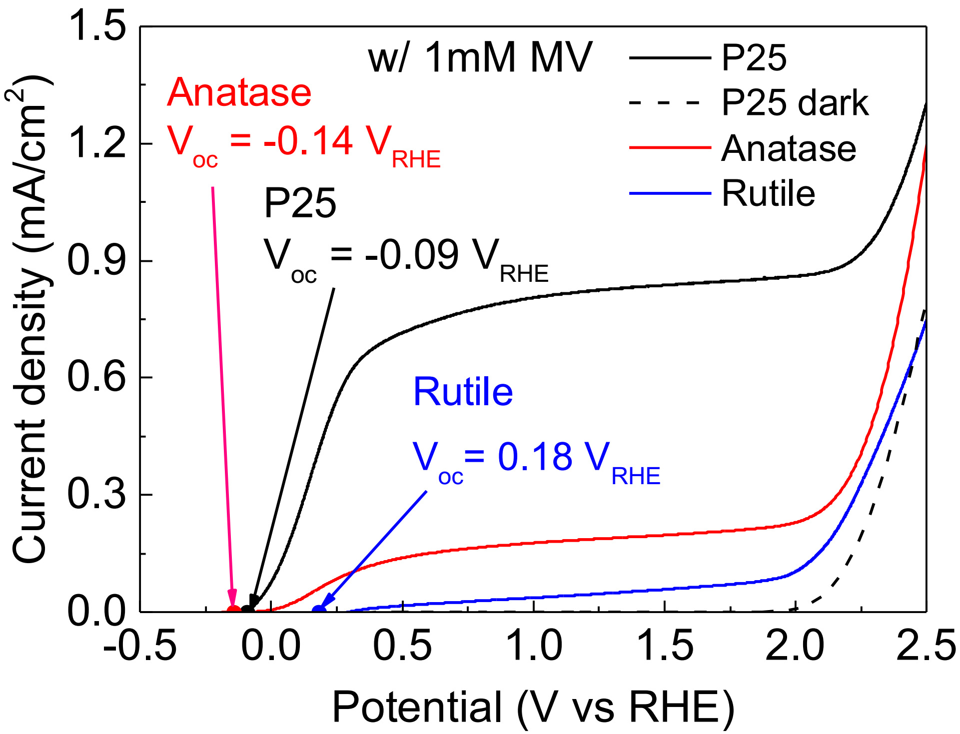

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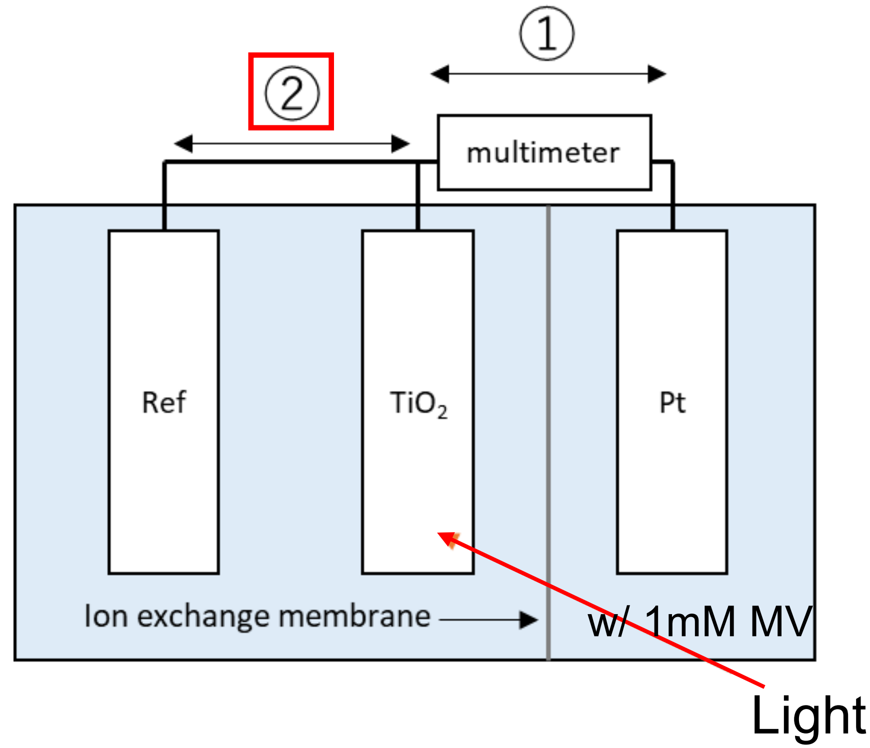

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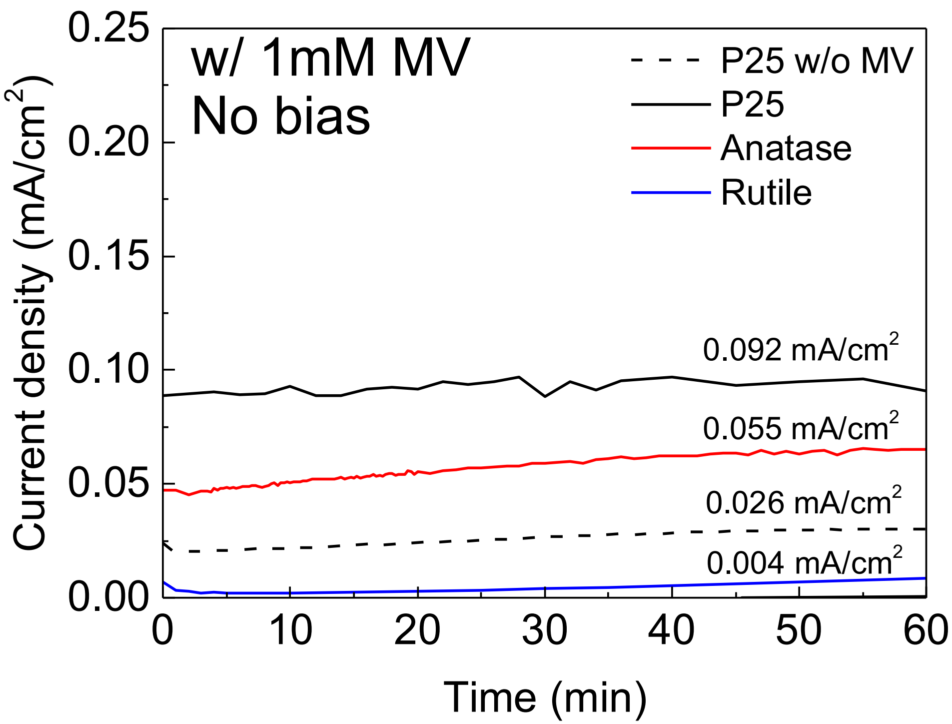
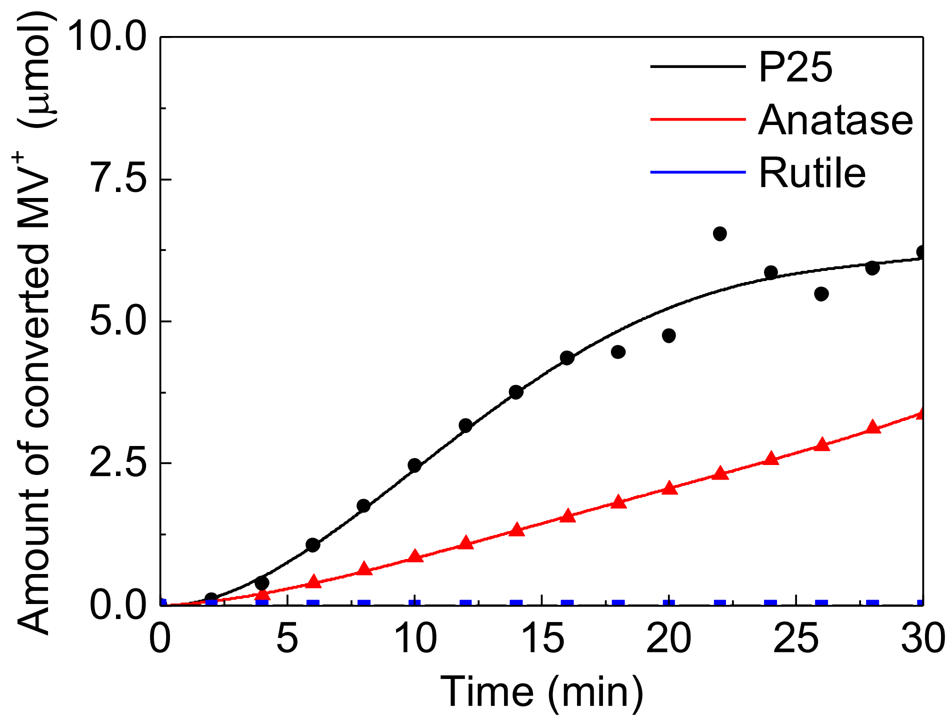
PEC reduction of MV in open-circuit condition

✓ I-t graph w/ light illumination



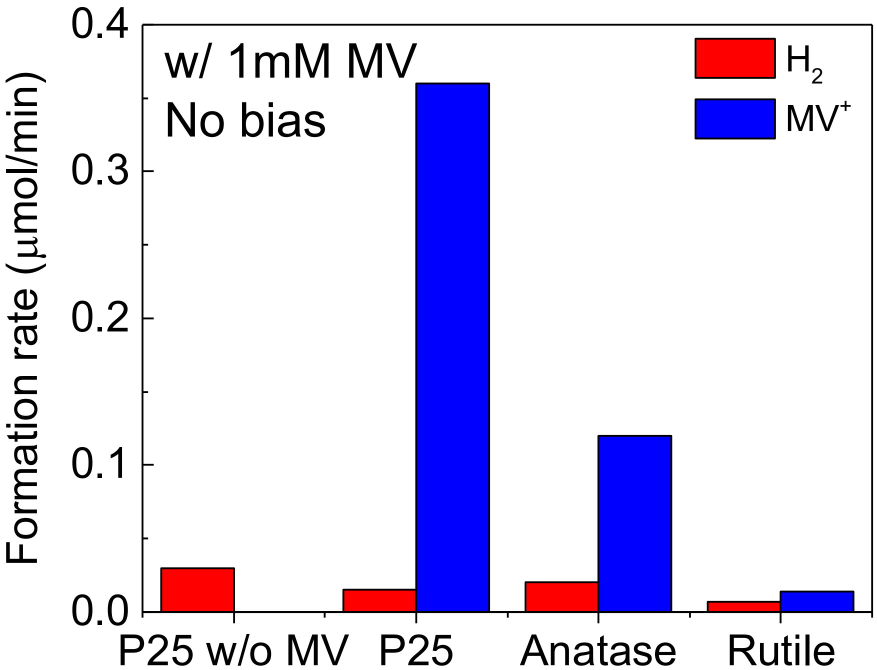
✓ Amounts of MV^+ production



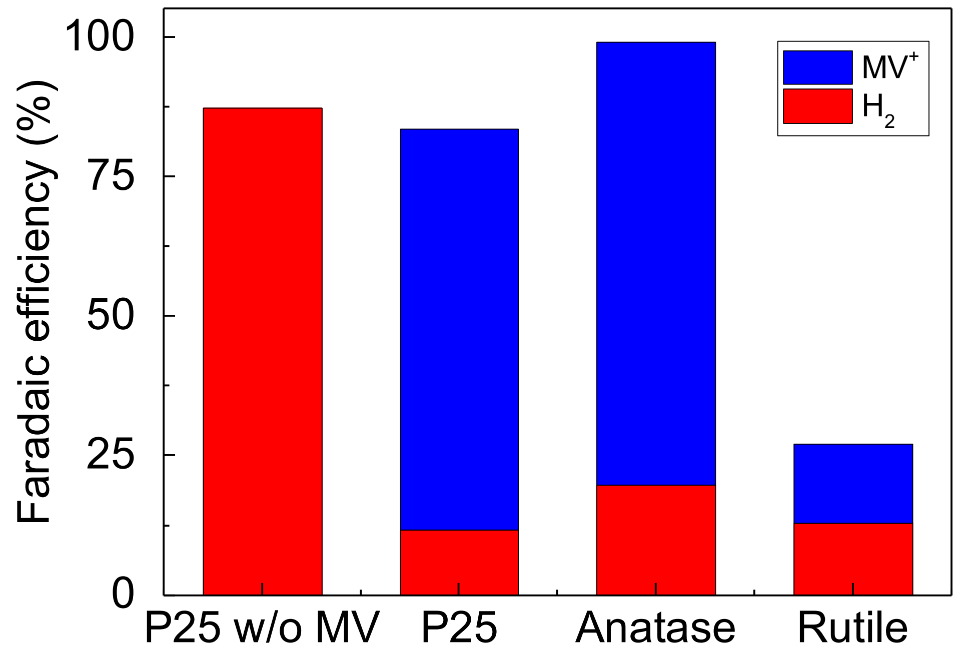
- For P25, 3.5 times higher current density is obtained w/ MV than w/o MV.
- <u>We confirmed MV^+ production by reducing MV^{2+} without external bias.</u>

PEC reduction of MV in open-circuit condition

✓ Production rate



✓ Products selectivity

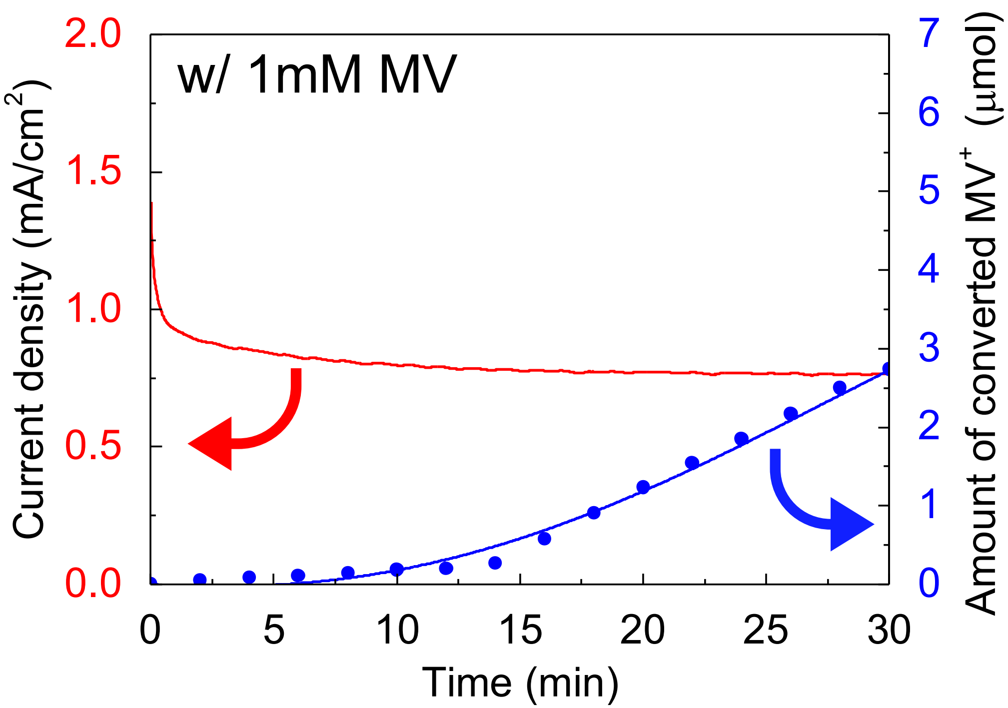


- P25 shows the highest MV^+ formation rate.
- MV reduction reduction is dominant under open-circuit condition.

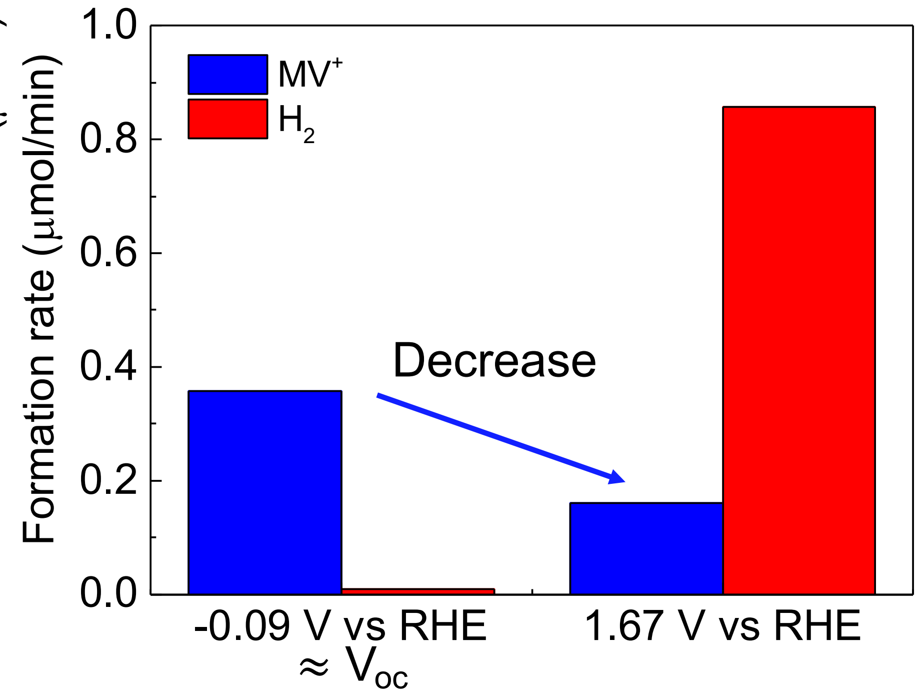
→ MV reduction potential should be lower than hydrogen evolving potential.

PEC reduction behavior of MV with external bias

✓ Photoelectrolysis at -1.7 V vs RHE



✓ Production rates comparison



- Applied bias boosts H_2 production while decreasing MV^{2+} reduction.

→ To selectively transfer electrons for MV reduction, controlling cathodic potential should be significant issue!

Summary

- MV is key element for electron transfers to biocatalysts for H_2 evolution.
- We approach PEC system for inorganic-bio water splitting.
- Electrochemical behavior of MV with Ag, Au, Ni, Pt has been investigated.
- PEC cell with P25 TiO_2 & Pt shows successful MV reduction without bias.
- Applied bias just boosts H_2 production while decreasing MV reduction reaction.
- Cathode potential should be properly controlled for preferential MV reduction toward biocatalytic H_2 production.

Thank you for your kind attention !