GCIM2024 Global Conference Innovation Materials 2024

Silicon Photocathode with Vertically Aligned TiO_2 Nanorods and Ni Catalyst for Enhancing Photoelectrochemical Nitrate Reduction to Ammonia

Hosted by MRS KOREA

Enok Lee and Sanghan Lee*

School of Materials Science and Engineering (SMSE)

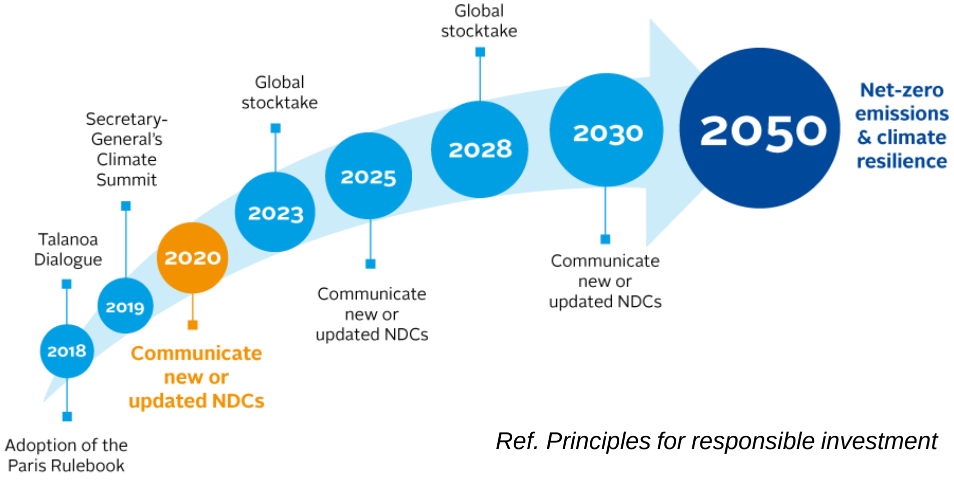
Gwangju Institute of Science and Technology (GIST)

GIST

SEED Sustainable Energy and Electronic Devices laboratory

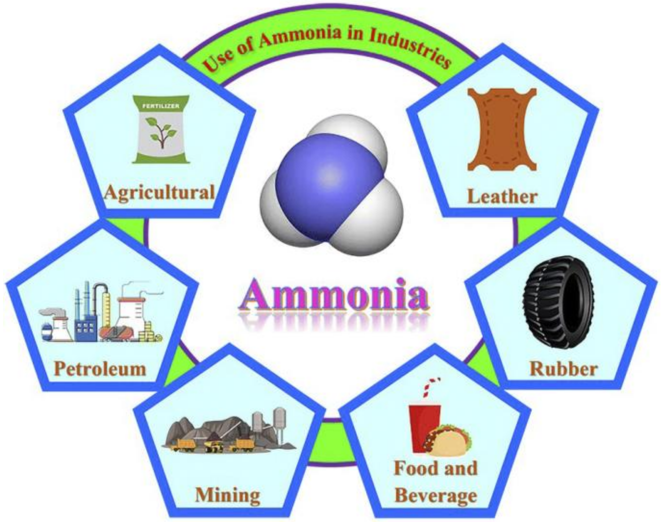
Contents

❖ Carbon neutrality



Ref. Principles for responsible investment

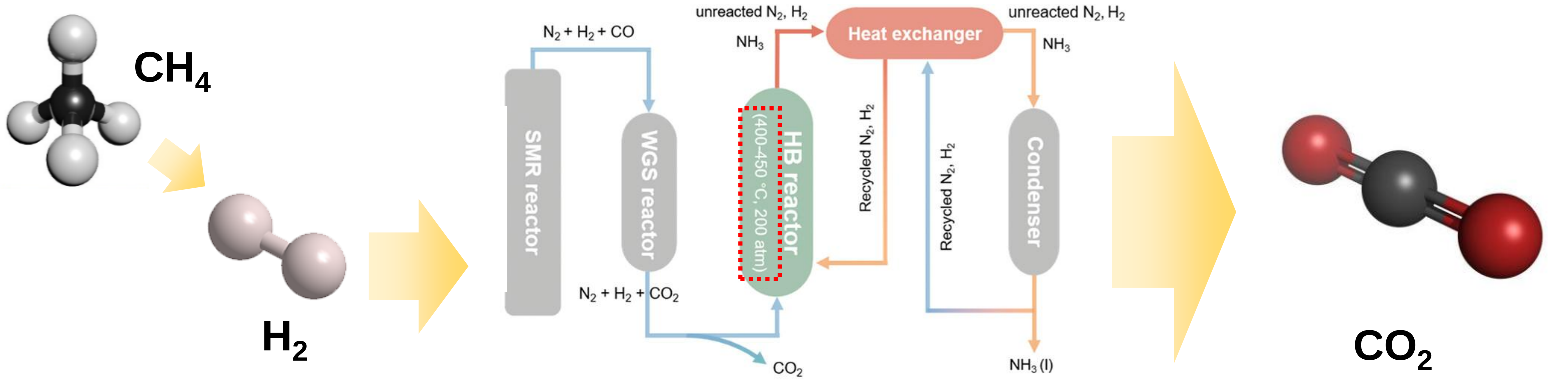
Ref. RSC Adv., **2023**, 13, 28211–28223.



- ✓ Essential compound in industry & agriculture
- ✓ Consumption of natural gas

Harbor-Bosch process

Ref. Adv. Mater.**2024**,36, 2304021



Considerable greenhouse gases emission

Ultimate goal

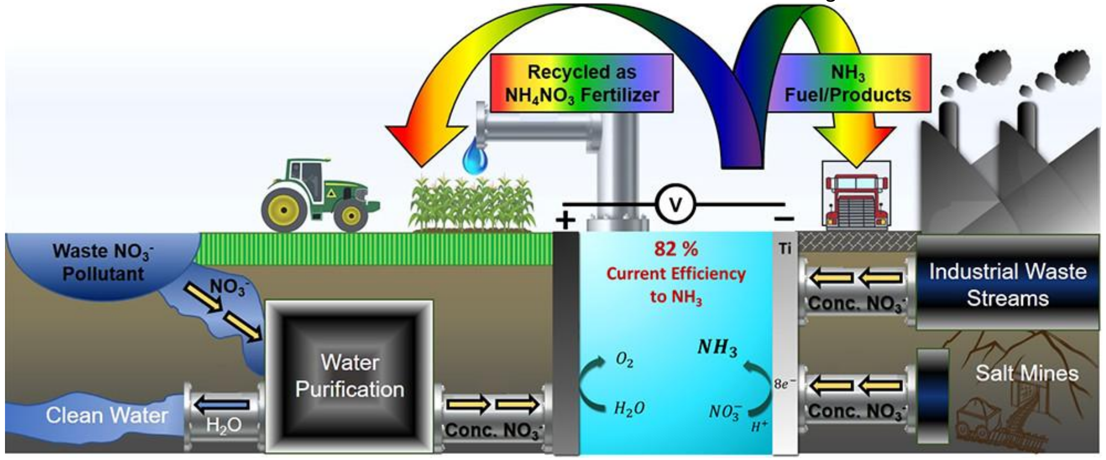
Fossil fuel independent method for NH_3 production

1. Introduction

❖ Eco-friendly catalytic ammonia synthesis

Electrochemical nitrate reduction reaction ($e\text{-}NO_3^-RR$)

Ref. *ACS Sustainable Chem. Eng.* **2020**, 8, 7, 2672–2681

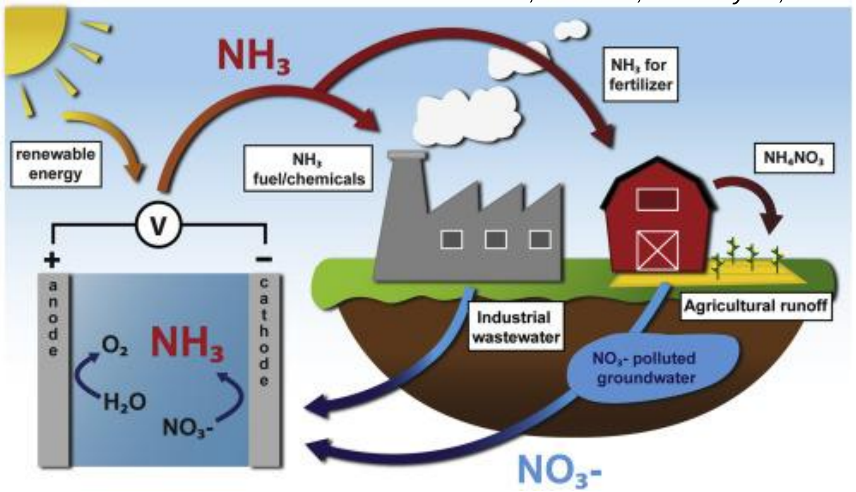


- ✓ Dual purposes of ammonia production & reuse of the waste nitrate
- ✓ High ammonia yield & ease of operation

However, $e\text{-}NO_3RR$ requires a high potential.

Photoelectrochemical nitrate reduction reaction (PEC NO_3^-RR)

Ref. *Joule* 5, 290–294, February 17, ***2021***



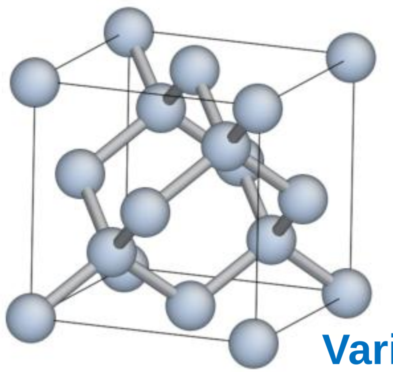
- ✓ The utilization of **solar energy**
- ✓ Reduction of the operation potential

The low yield rate & selectivity remain bottlenecks.

GIST

1. Introduction

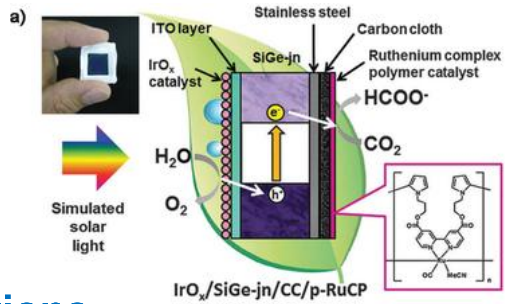
❖ Silicon (Si) photoelectrodes



[Silicon]

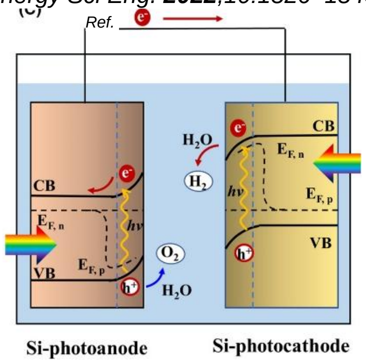
Various applications

Ref. *Energy Environ. Sci.*, **2015**,8, 1998-2002



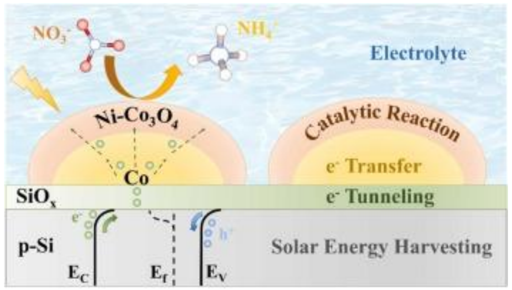
[PEC CO_2 reduction]

Ref. *Energy Sci Eng*. ***2022****;10:1526–1543*



[PEC water splitting]

Ref. Appl. Catal. B. 351 (**2024**) 123980



[PEC NO_3^-RR]

Advantage

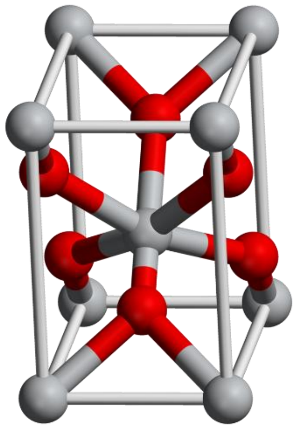
- ✓ Narrow band gap (1.12 eV)
  → High photocurrent density
- ✓ Excellent charge carrier mobility
- ✓ Mature fabrication

Drawbacks

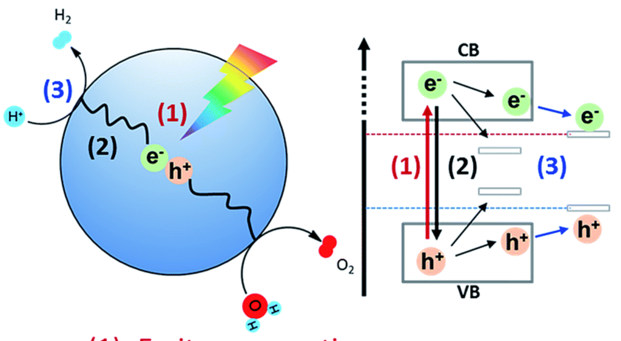
- ✓ Insufficient photovoltage
- ✓ Chemical corrosion in aqueous electrolytes
- ✓ Sluggish charge-transfer kinetics
- ✓ High light reflection

So, passivation layer & Catalysts are required.

❖ Titanium dioxide (TiO_2)



Ref. J.Mater. Chem. A, ***2019***, *7, 13833-13859*

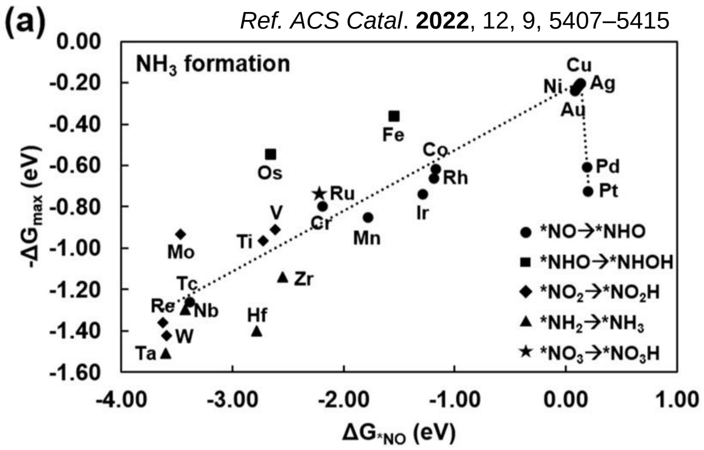


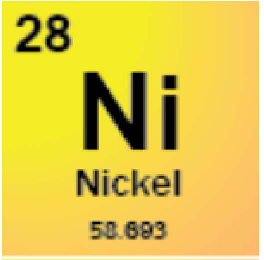
(1): Exciton generation
(2): Exciton separation and transfer
(3): Interfacial charge transfer to water

- ✓ Ultra-Violet light absorption capability
- ✓ Efficient anti-reflection
- ✓ Appropriate band offset with silicon

❖ Nickel (Ni) catalyst

Ref. ACS Catal. **2022**, 12, 9, 5407–5415

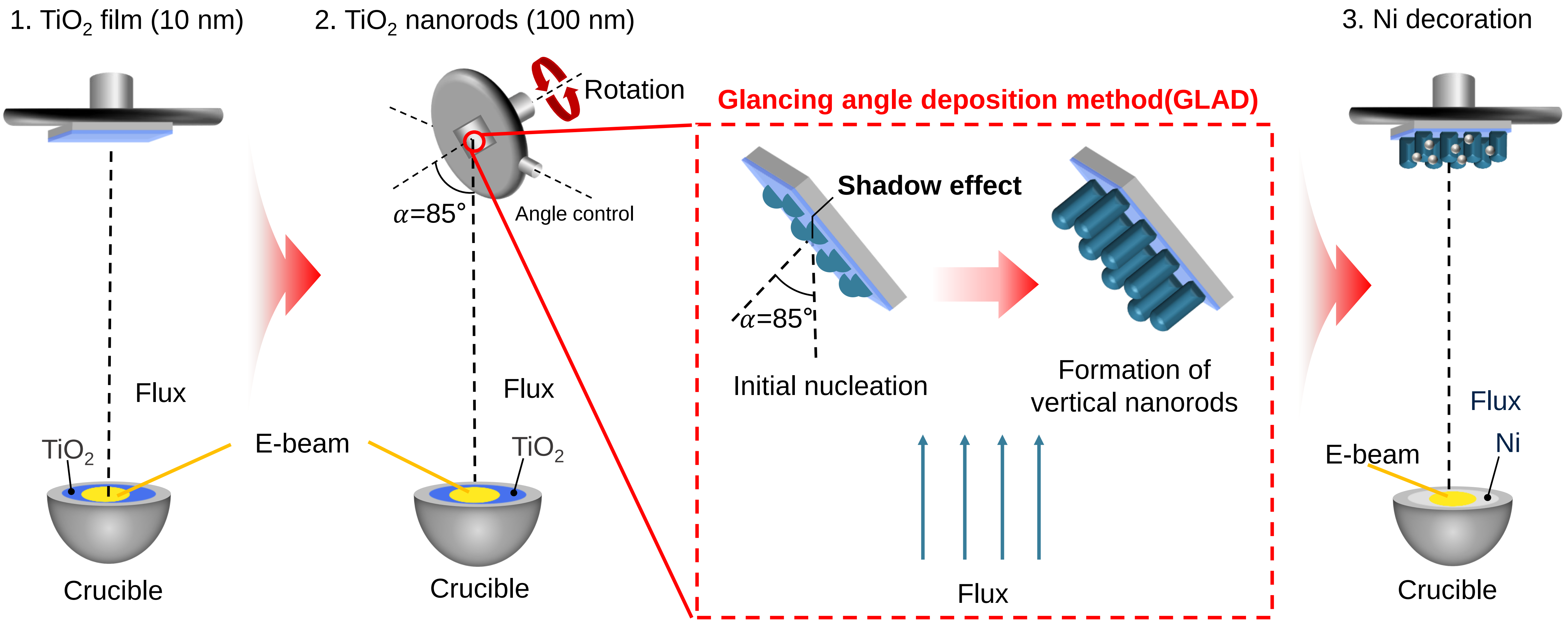




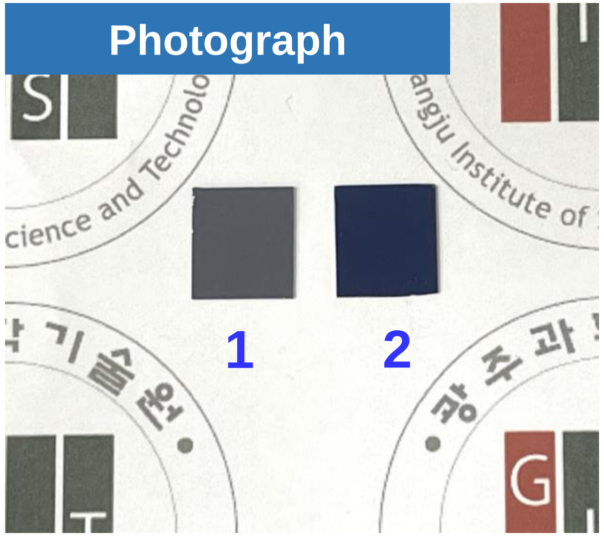
- ✓ Cost effectiveness
- ✓ Stable in alkaline electrolyte
- ✓ Reaction kinetic improvement

TiO_2 nanorods + Ni catalyst → **“ Enhancing PEC NO_3^-RR ”**

❖ Sequential deposition by e-beam evaporator

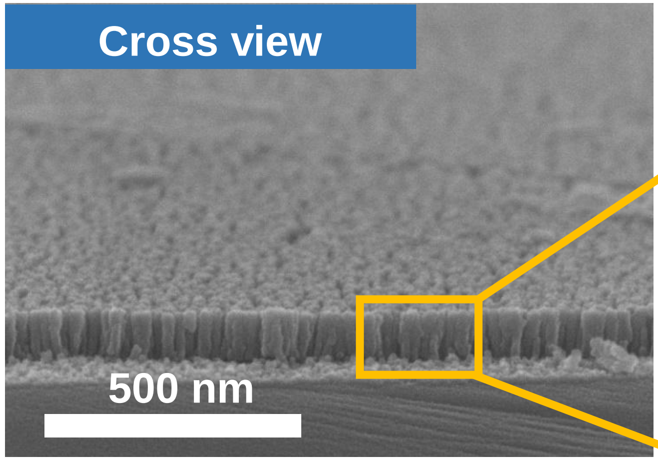


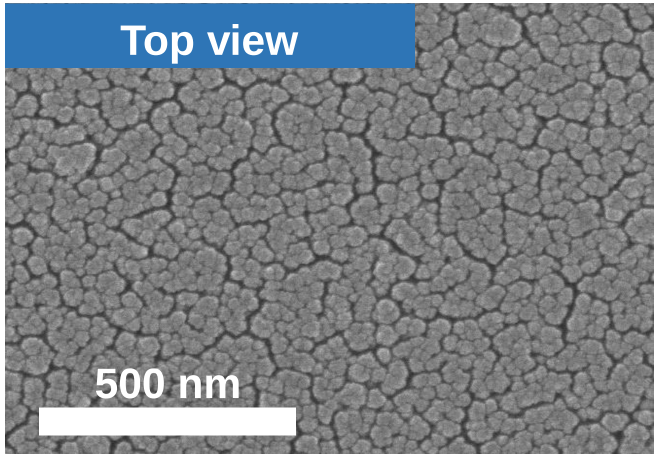
❖ **Surface morphology analysis (Scanning Electron Microscope (SEM) images)**

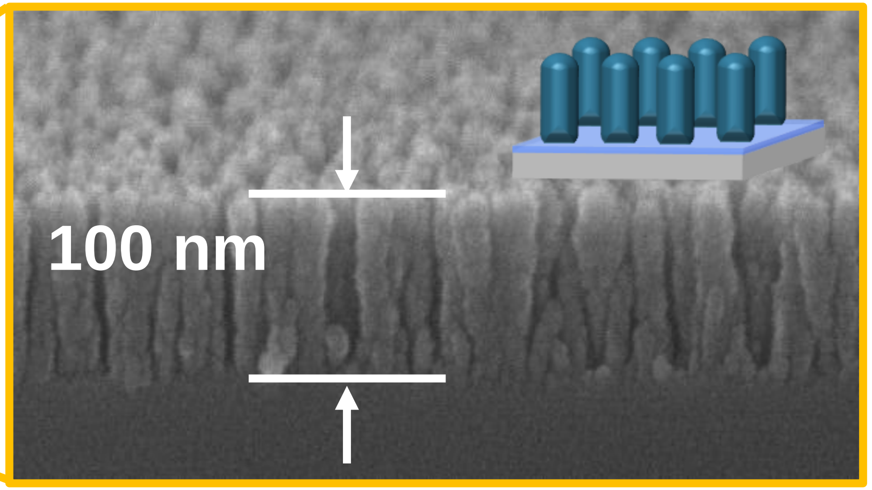


1: Bare p-Si

2: TiO_2 NRs/ TiO_2 film/ p-Si





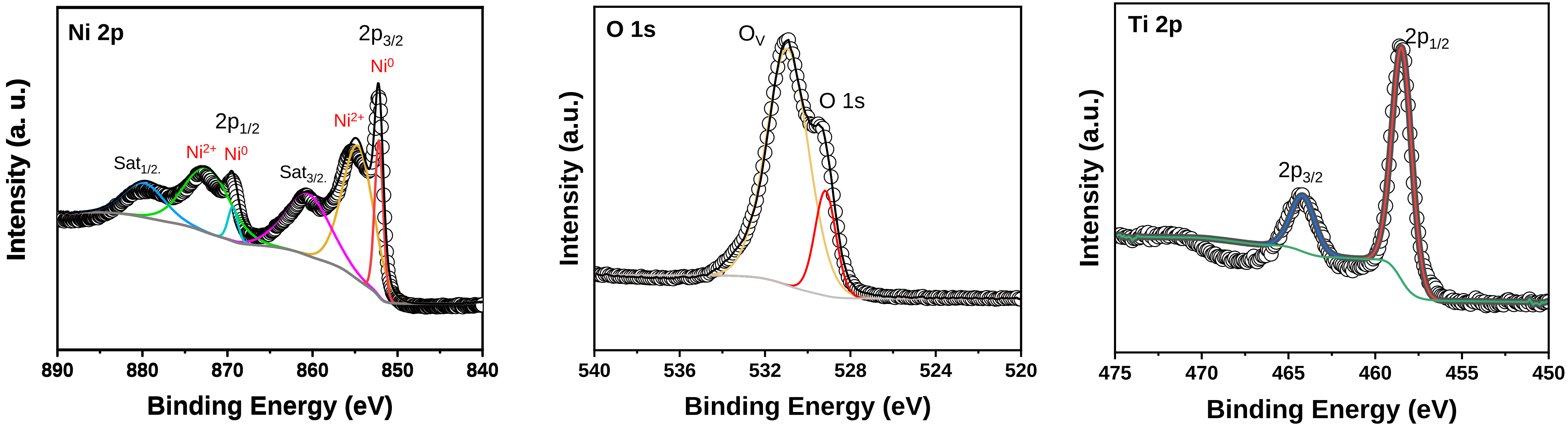


- ✓ Vertically aligned TiO_2 nanorods (NRs)
- ✓ Uniform length: 100 nm
- ✓ Porous surface morphology

✓ **The vertically grown TiO_2 NRs exhibited uniform length and porosity.**

3. Results

❖ **Structural characterizations (X-ray photoelectron Spectroscopy (XPS))**



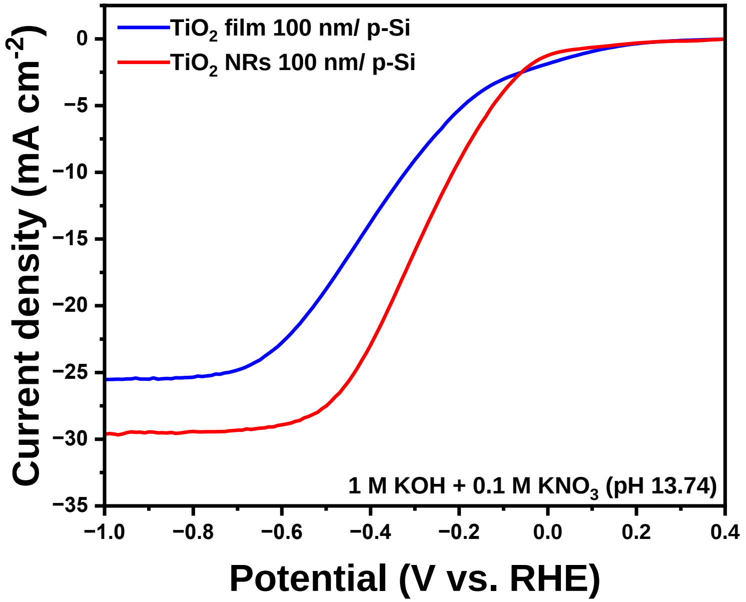
✓ **Ni catalysts is embedded in the TiO_2 NRs.**

✓ **The abundant surface oxygen vacancies can further enhance the catalytic activity.**

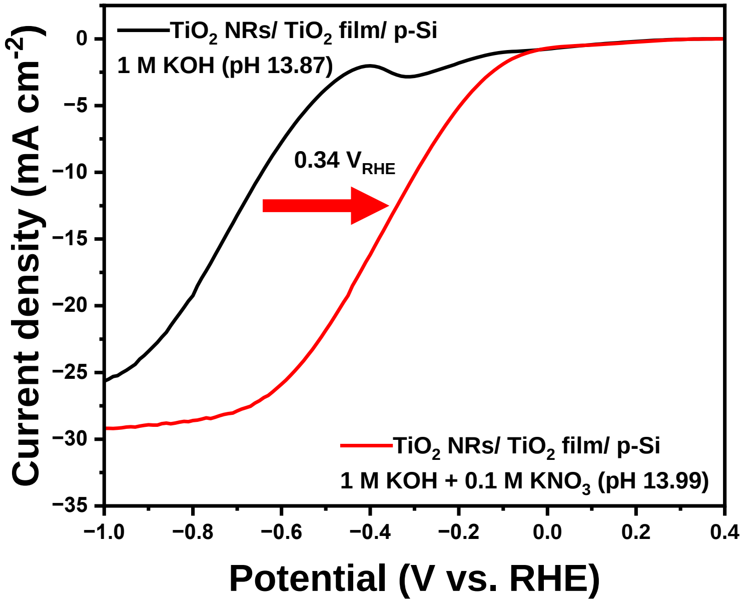
3. Results

❖ PEC performances for NO_3^-RR (TiO_2 NRs/ TiO_2 film/ p-Si photocathode)

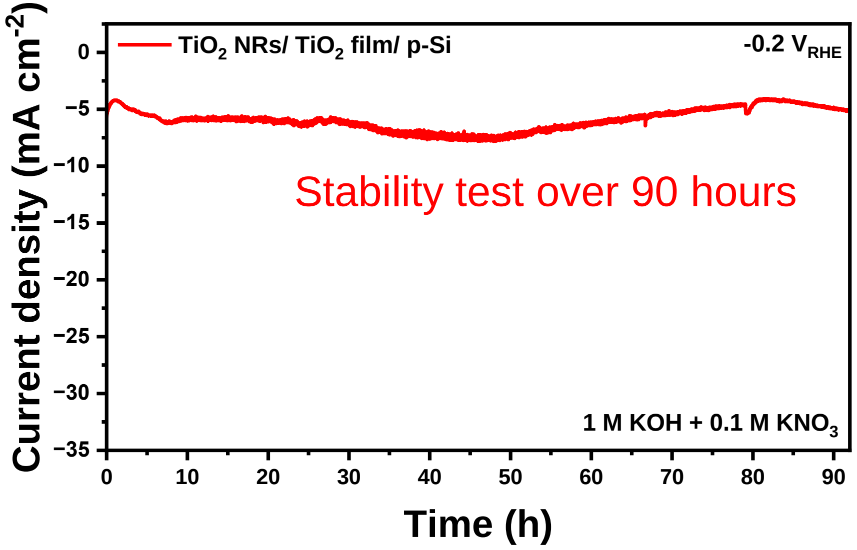
Film 100 nm *vs.* NRs 100 nm



w. KNO_3 *vs.* w/o. KNO_3



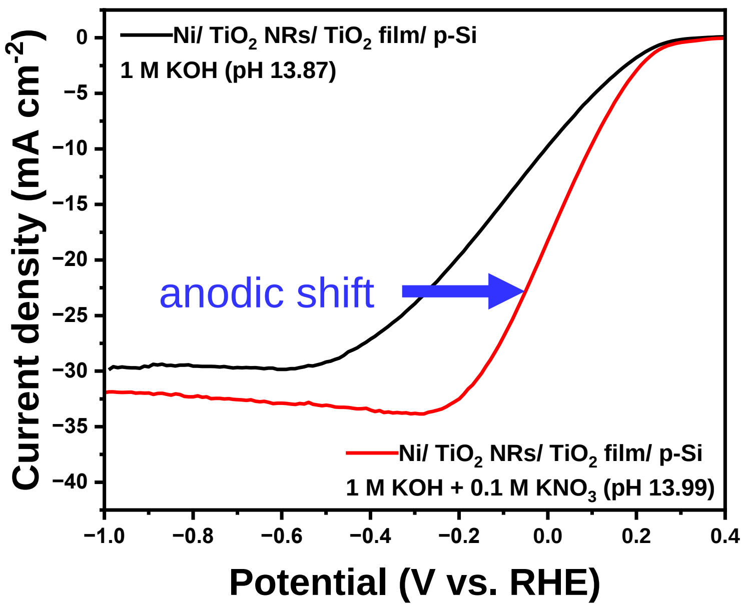
Stability test



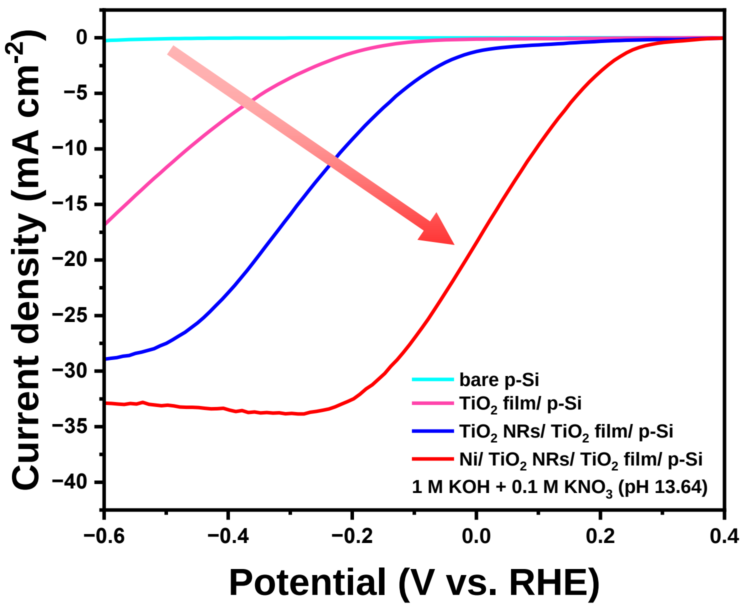
✓ **The Si photocathodes with TiO_2 NRs exhibited good PEC performance for PEC NO_3^-RR.**

❖ PEC performances for NO_3^-RR (Ni/ TiO_2 NRs/ TiO_2 film/ p-Si photocathode)

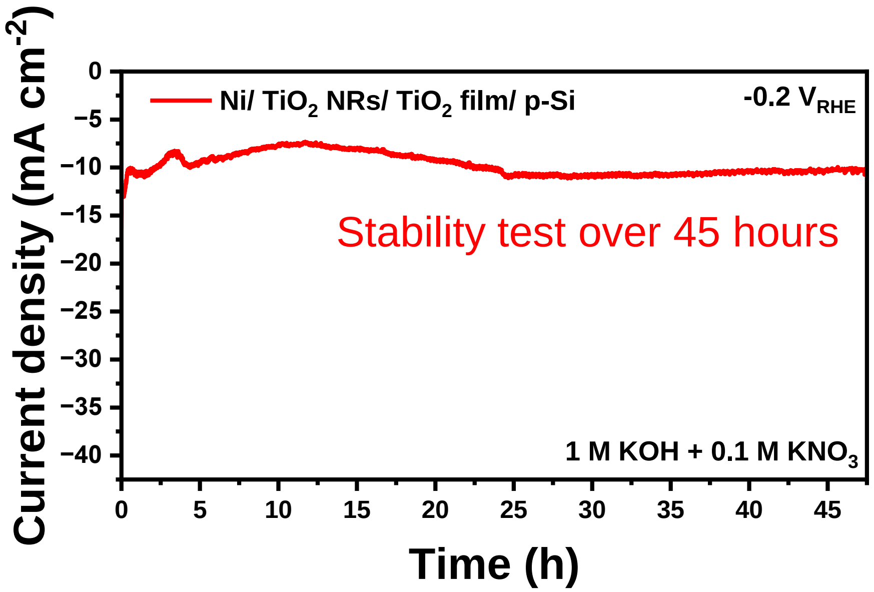
w. KNO_3 *vs.* w/o. KNO_3



Effect of TiO_2 layer



Stability test

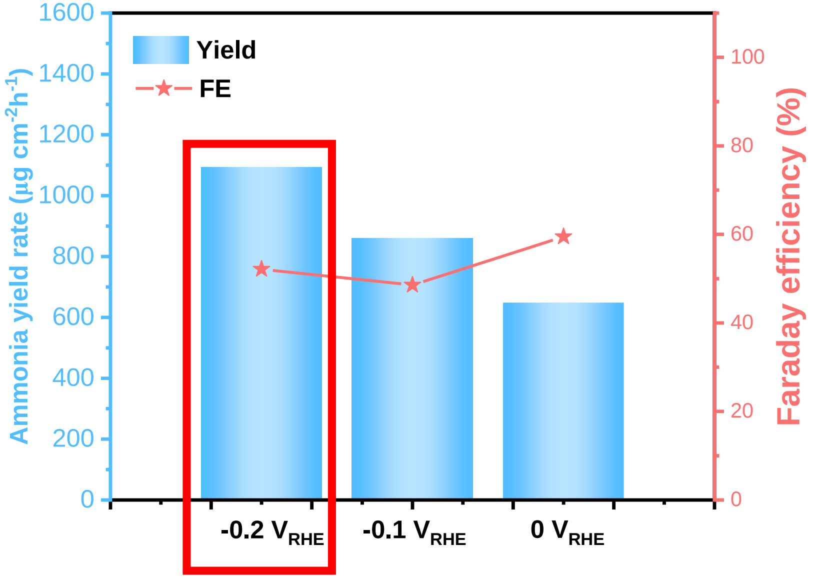


✓ **Ni catalysts enhanced PEC NO_3^-RR with an onset potential of 0.28 V_{RHE}.**

3. Results

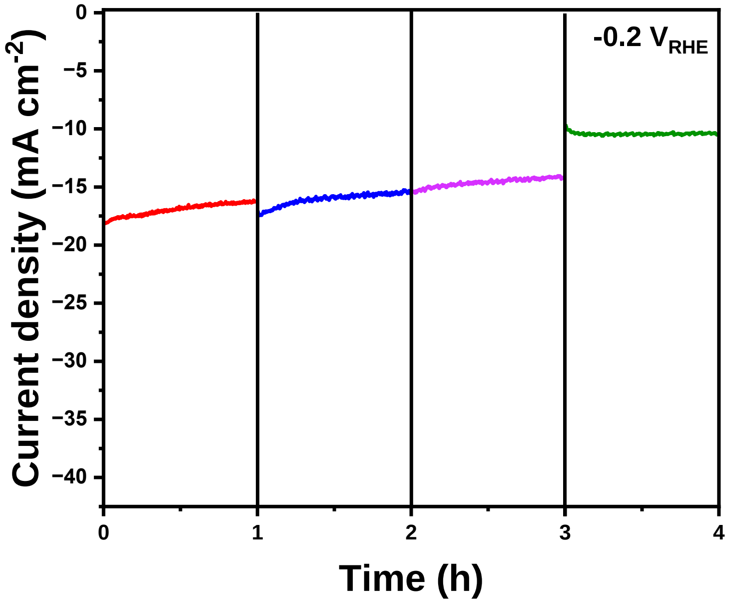
❖ **Quantitative analyzation for PEC NO_3^-RR**

NH_3 yield & FE%

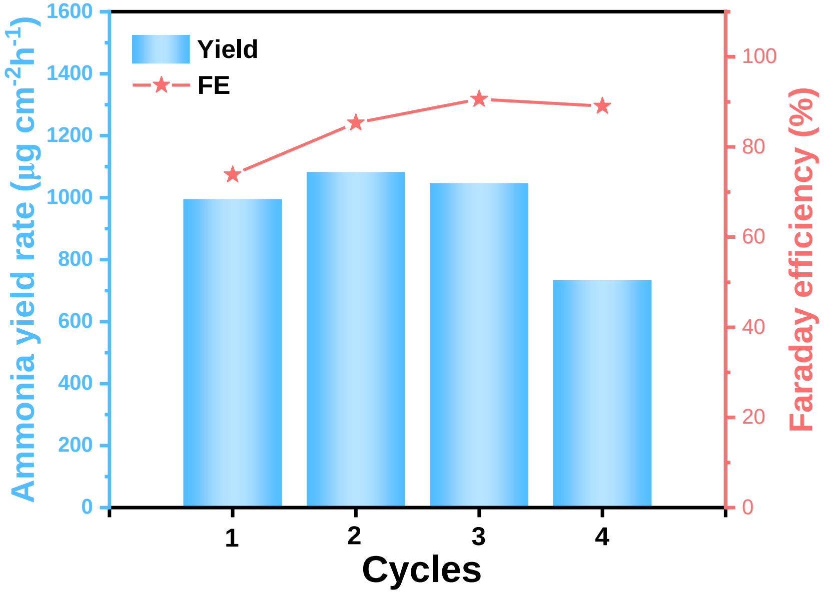


Highest NH_3 yield

Chronoamperometry curves



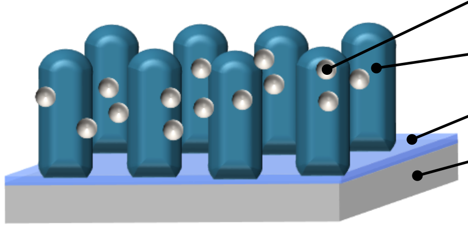
Cycling test



✓ **At -0.2 V_{RHE}, a Faradaic efficiency of 90.6% and a yield of 1046.6652 μg/h cm^2 were achieved.**

GIST

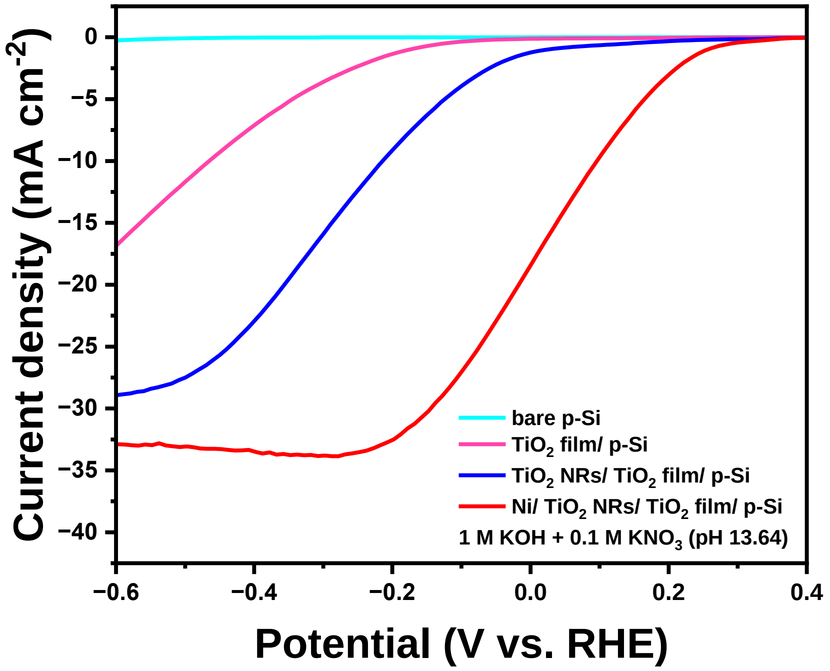
4. Summary



- ✓ Using GLAD method by e-beam evaporator, we fabricated silicon photocathode with **vertically aligned TiO_2 nanorod arrays and nickel.**

- ✓ The decorated Ni on vertically aligned TiO_2 nanorod arrays completely **increased the reaction surface area** and the **enhanced photo-absorption** was enabled by the anti-reflection of the 1D nanorod structure.

- ✓ It showed photocurrent of **31.8 mA cm^{-2} at -0.2 V_{RHE}** and positive onset potential of **0.28 V_{RHE} and 1046 ug/h cm^2 ammonia yield.**



Thank you
for your attention

E-mail: enok2257@gm.gist.ac.kr

GIST

SEED

Sustainable Energy and Electronic Devices laboratory