제 31회 한국반도체학술대회
The 31st Korean Conference on Semiconductors

GIST SEED
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KCS 2024 - Device for Energy

Enhancing $BiVO_4$ Photoanode Performance by Insertion of an Epitaxial $BiFeO_3$ Ferroelectric Layer

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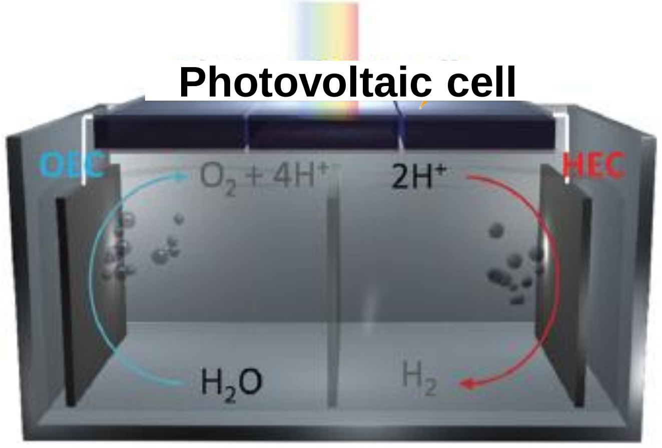
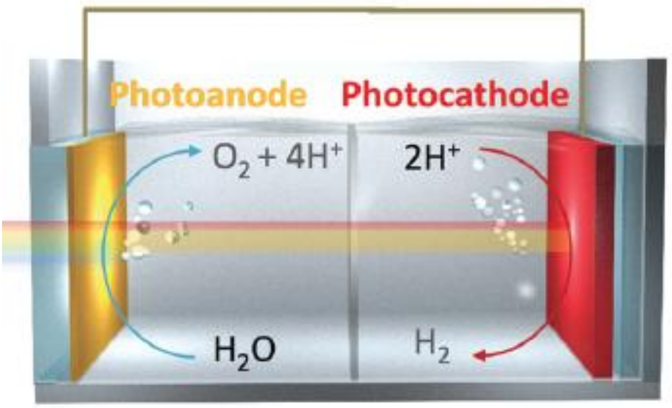
❖ Photo-assisted water splitting systems

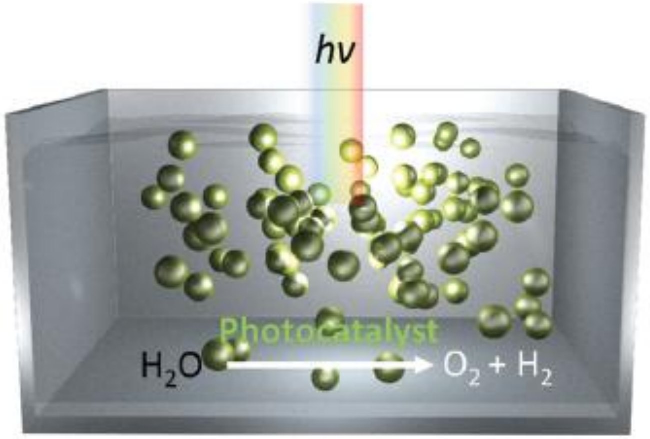
Photovoltaics-electrolysis (PV-EC)



Photoelectrochemistry (PEC)



Photocatalysis (PC)



ref. Kim *et al.*, Chem. Soc. Rev., **48**, 1908 (2019)

High efficiency

BUT

Complex system (high cost)

Suitable system for H_2 production

Simple system (low cost)

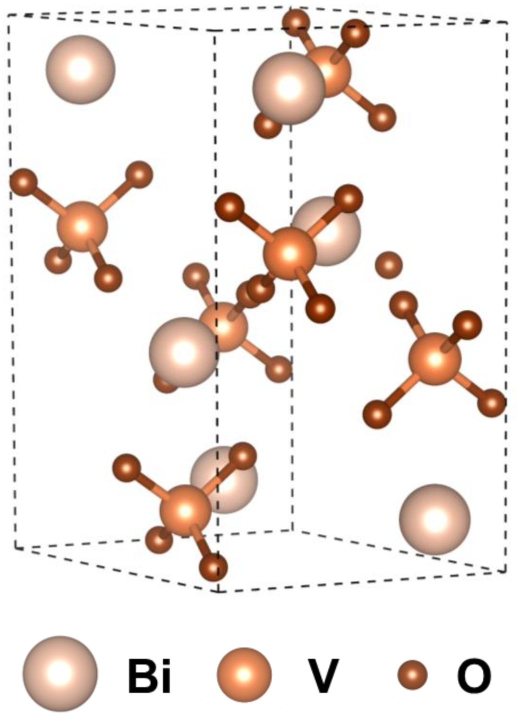
BUT

Low efficiency

Introduction

❖ Bismuth vanadate ($BiVO_4$, BVO)

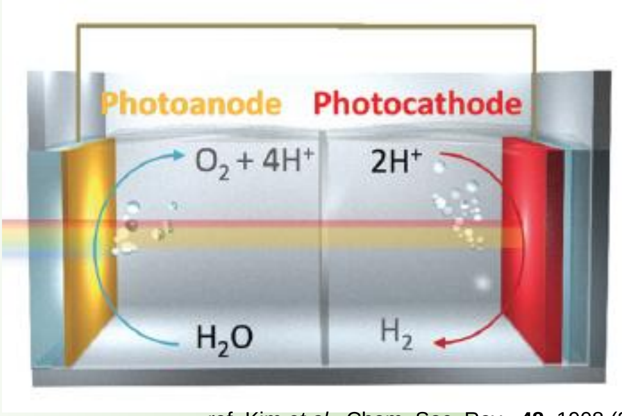
$BiVO_4$ (BVO)



Advantages

- Narrow direct band gap (2.4–2.6 eV)
- Favorable band position for water splitting
- Chemical stability in neutral electrolytes
- High theoretical solar-to-hydrogen (STH) efficiency (~9.2%)
- Earth abundant resources

Suitable for photoelectrochemistry



ref. Kim *et al.*, Chem. Soc. Rev., **48**, 1908 (2019)

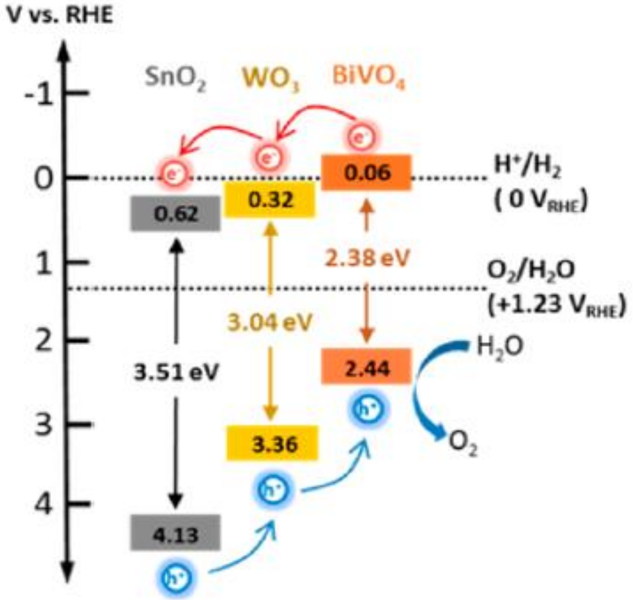
Drawback

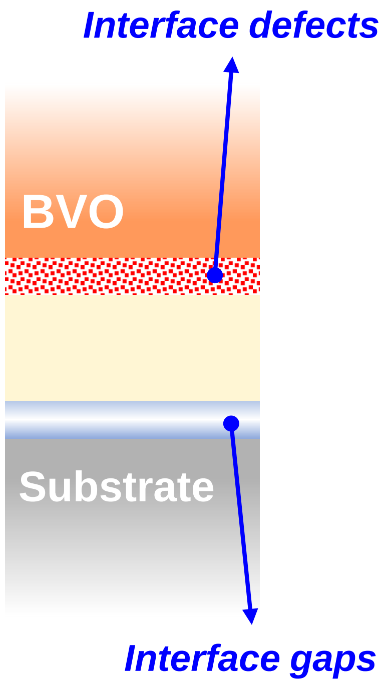
- High charge recombination rate
- Slow charge transfer

Huge obstacle to achieve ideal performance of BVO

Introduction

❖ Type-II heterostructure

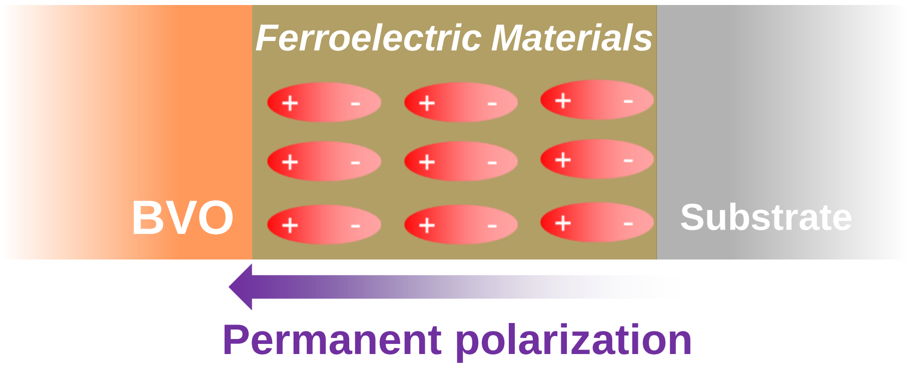




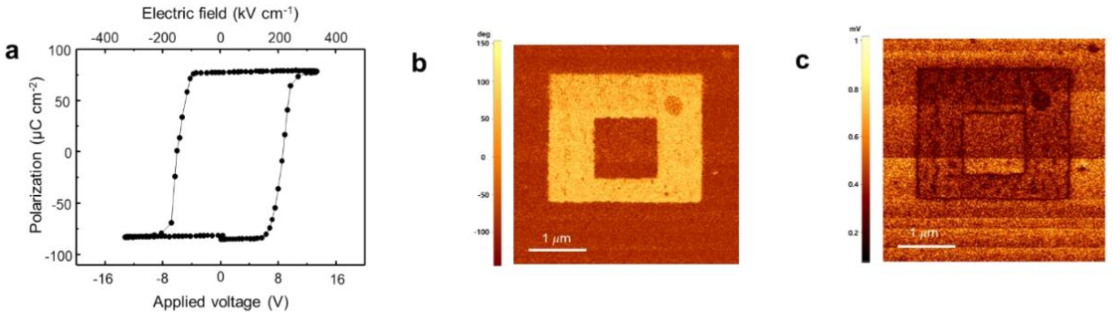
ref. ACS Appl. Mater. Interfaces., **9**, 1479, 2017.

- **Built-in electric field** due to staggered band alignment
- However, inevitably limited by **irregular interfaces of junctions** that are difficult to control

❖ Ferroelectric Materials



- **Strong** and **interface-independent** field
- Spontaneous polarization (self-polarization) in **epitaxial thin films of ferroelectric material**

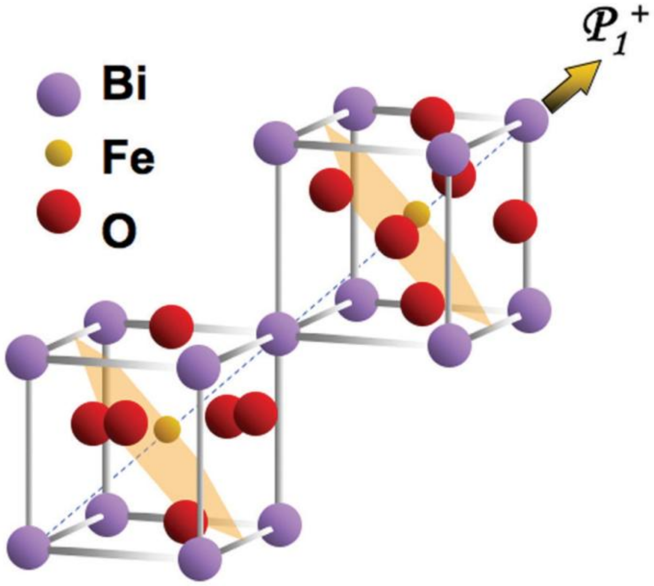


ref. Adv. Mater. 2022, 34, 2203097.

Introduction

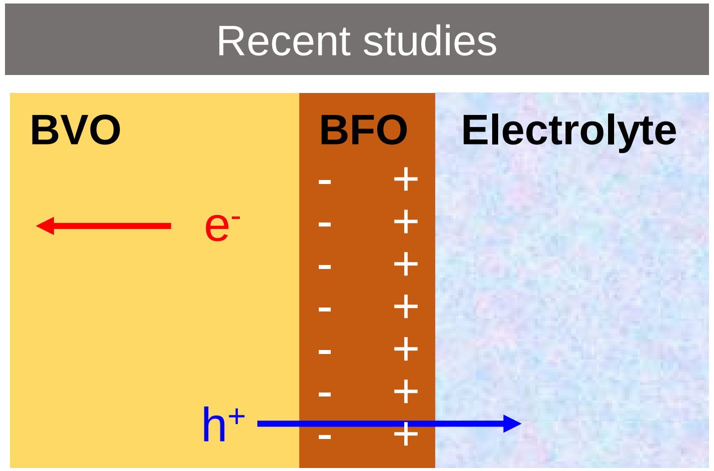
❖ Bismuth ferrite ($BiFeO_3$, BFO)

Non-centrosymmetric crystal structure → Permanent polarization

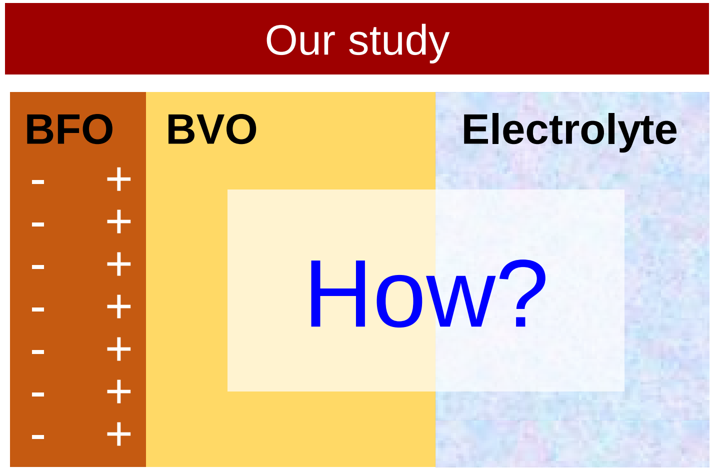


ref. Materials Today. 2007, 10, 16.

- Strong polarization field (~90 μC cm^{-2}) and high T_c (1103 K)
- Relatively narrow direct bandgap
- Suitable band position for water splitting *vs.* other ferroelectric materials



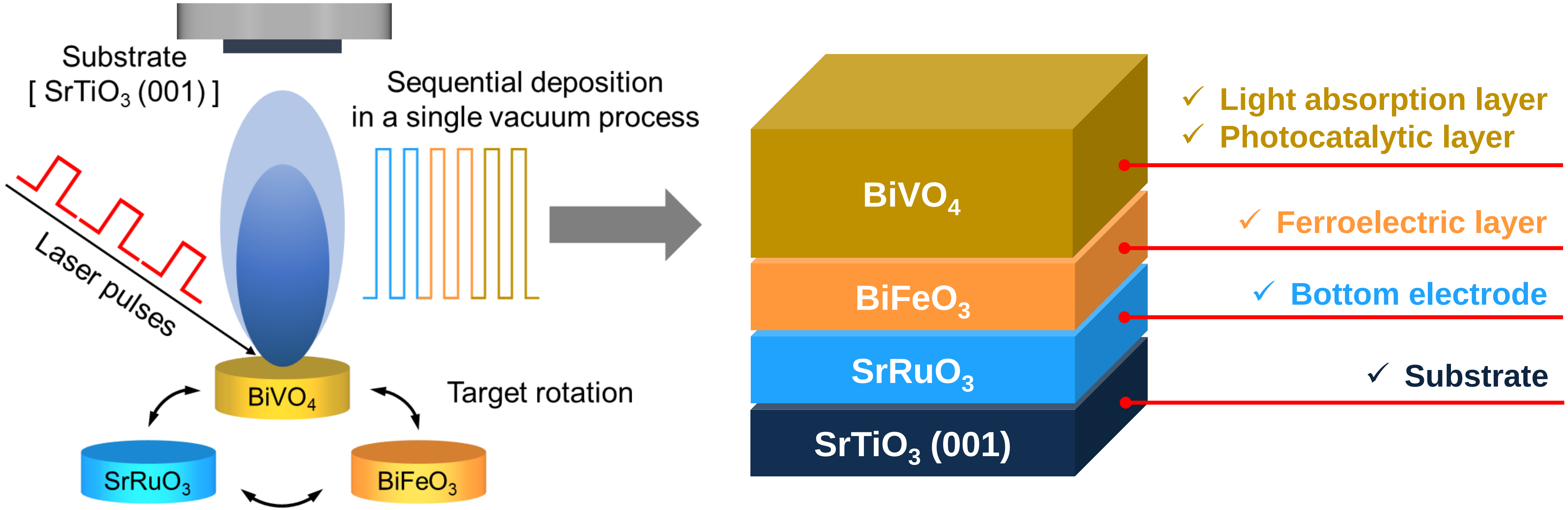
- Polycrystalline BFO thin films
- Dominant effects of type-II heterojunction



- Introducing epitaxial BFO thin films
- Dominant effect of self-polarization of BFO
- Potential for co-catalyst adoption

Methods

❖ **Pulsed laser deposition(PLD) system**

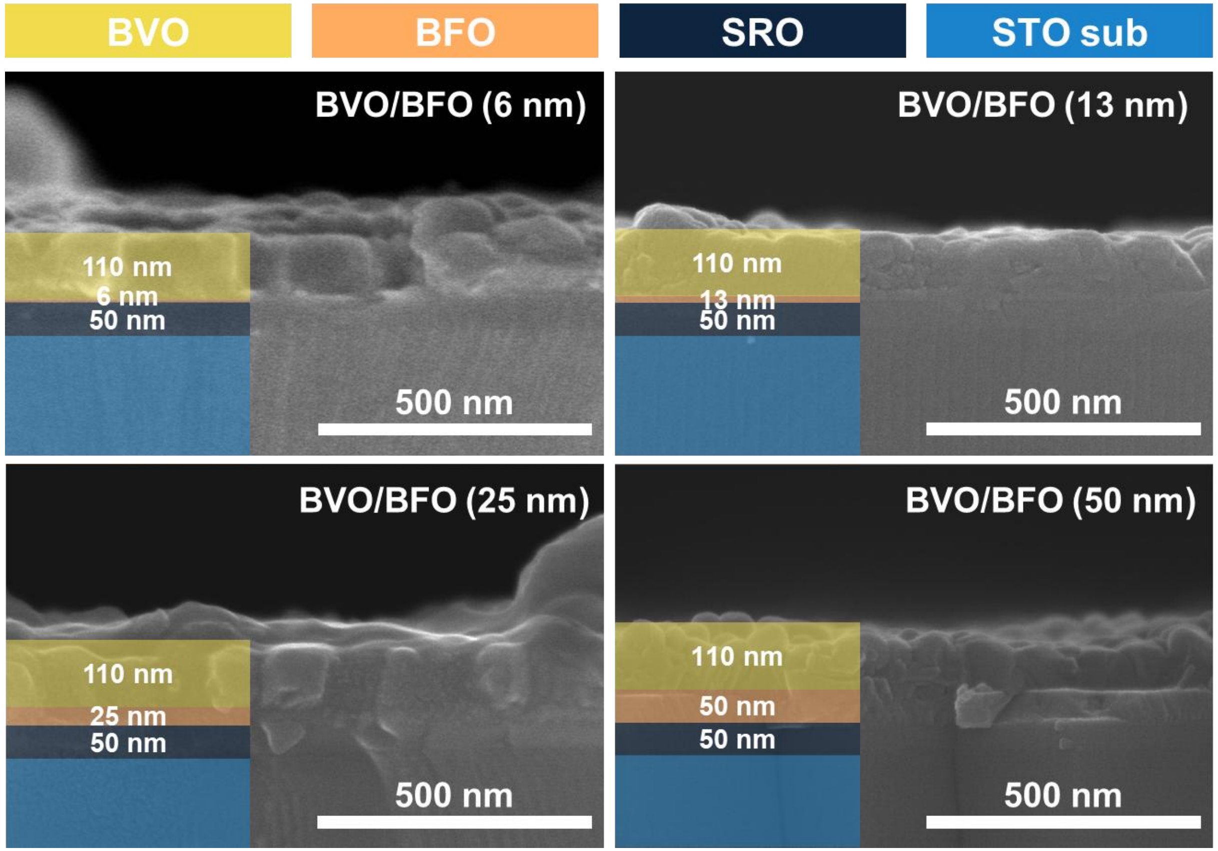


- High-quality and epitaxial thin film growth of various oxides
- in-situ deposition of heterostructures

Results

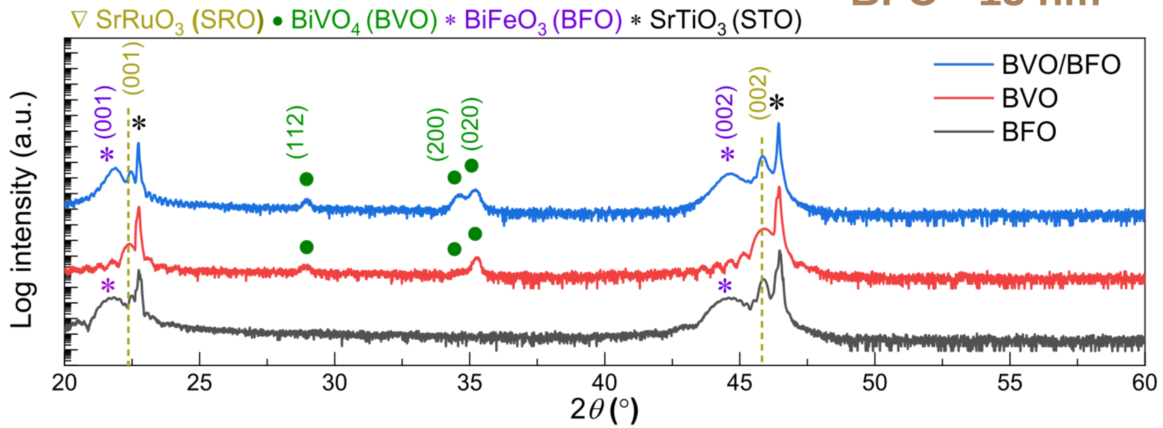
❖ Structural analysis

Scanning electron microscopy (SEM) images



X-ray θ-2θ diffraction pattern

BVO - 110 nm
BFO - 13 nm

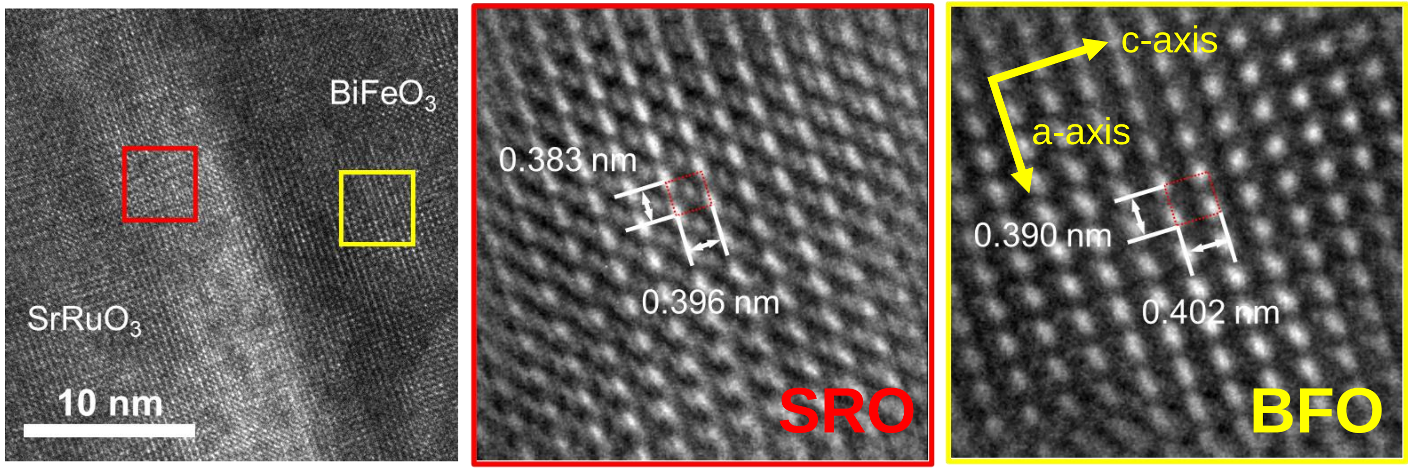


- ✓ Various thicknesses of BFO thin films controlled by the number of laser pulses
- ✓ **Epitaxially grown BFO/SRO thin films on the STO (001) substrate**
- ✓ Polycrystalline BVO thin films

Results

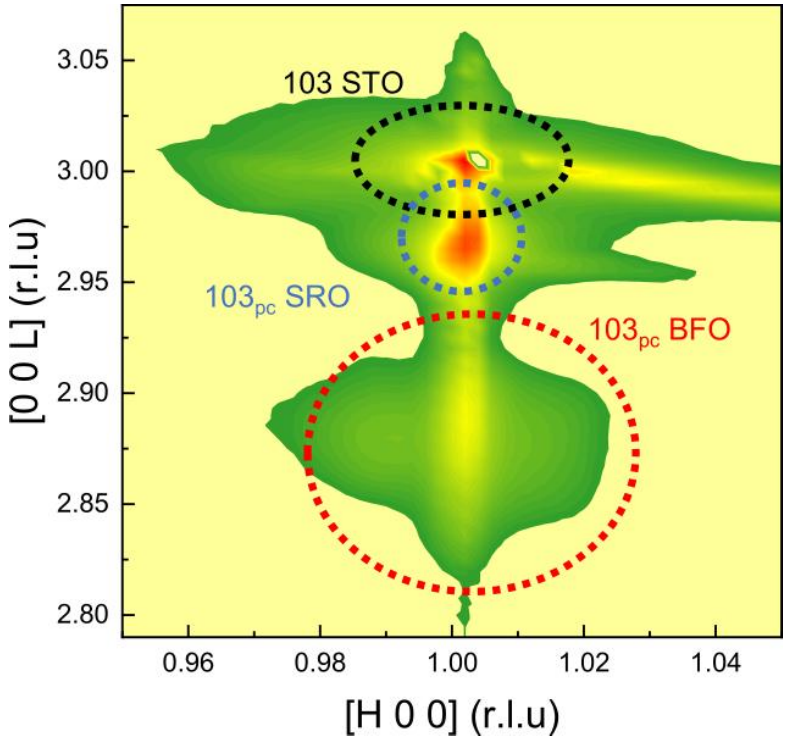
❖ Structural analysis

HR-TEM images



	HR-TEM	XRD-RSM	theoretical
c(BFO) (Å)	4.02	4.06	3.96
a(BFO) (Å)	3.90	-	3.96

XRD reciprocal space mapping (RSM)



BFO/SRO/STO

in-plane compressive strain

c-axis → **Elongation**

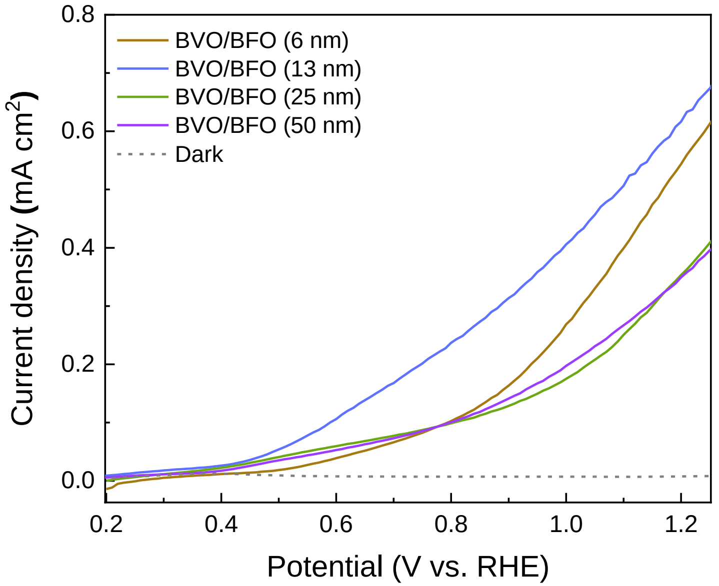
a-axis → **Shrinking**

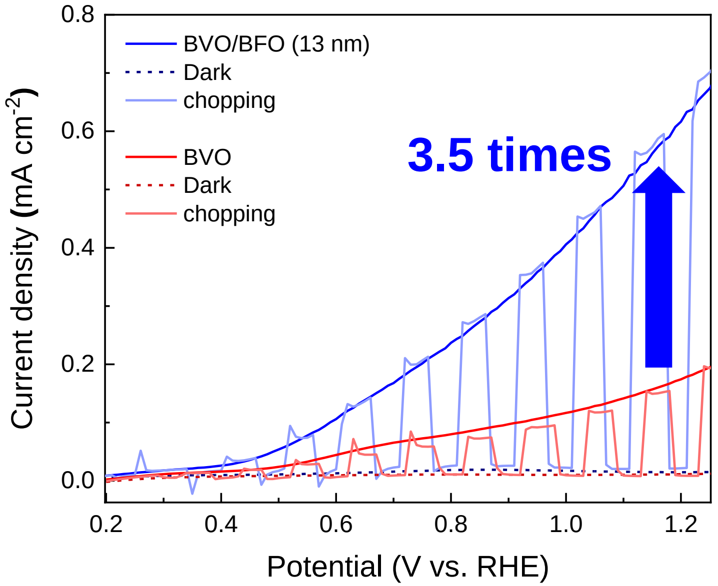
Ferroelectric properties !!

Results

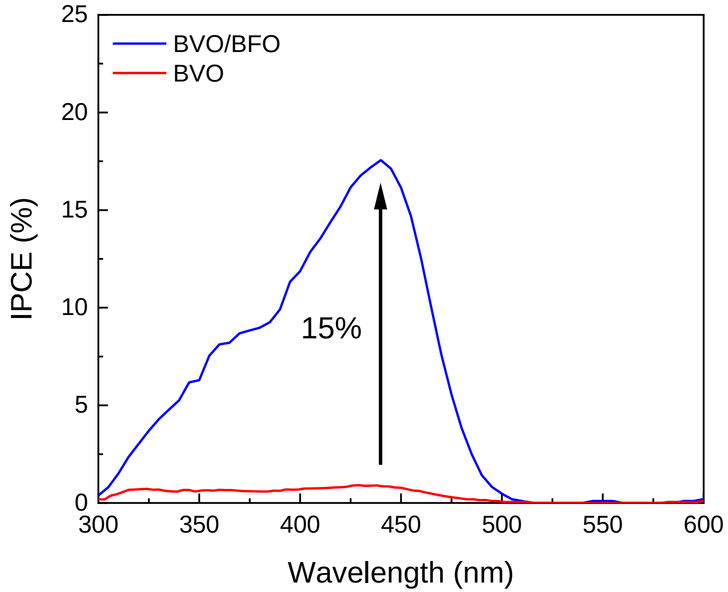
❖ Photoelectrochemical measurement

Linear sweep voltammetry (LSV) curves





Incident photon-to-current efficiency (IPCE)

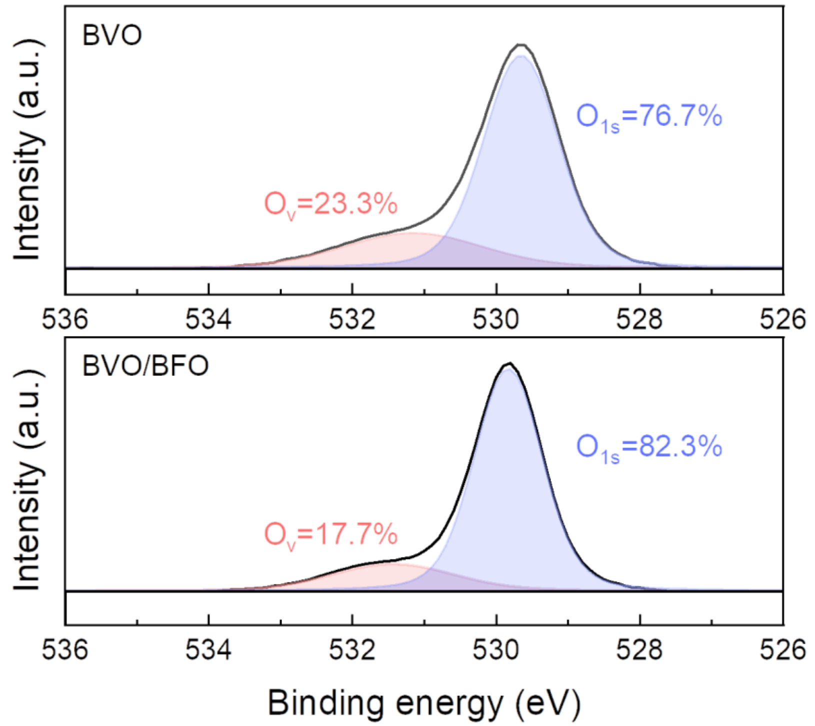


- The BVO/BFO (13 nm) photoanode shows the highest photocurrent density.
- The BFO/BVO photoanodes exhibited about **3.5 times higher photocurrent density** of 0.65 mA cm^{-2} at 1.23 V_{RHE} compared to that of the bare BVO photoanodes.
- The IPCE value increases (> 15%) at around 450 nm, which corresponds to the band gap of the BVO.

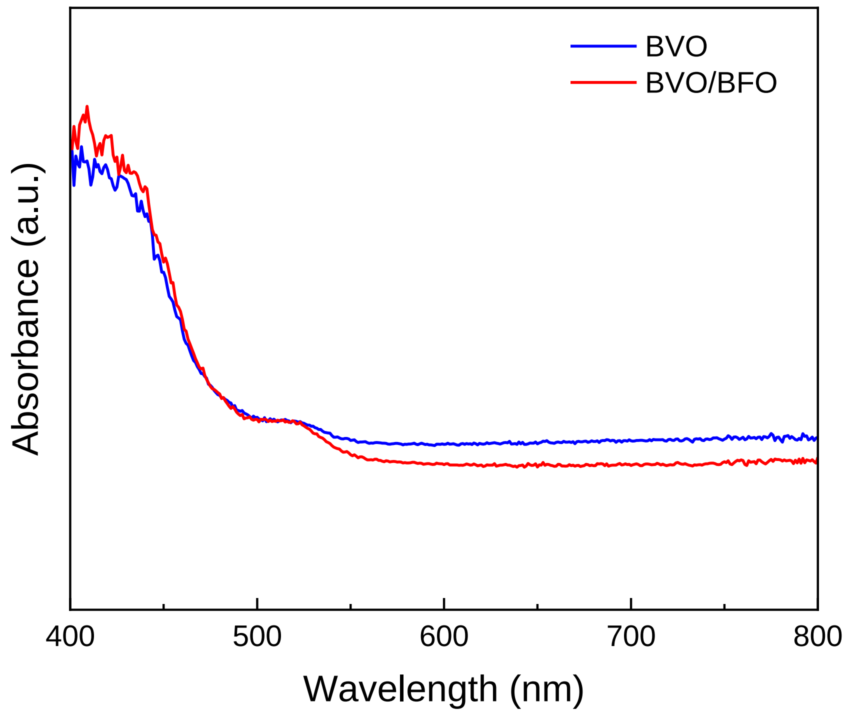
Results

❖ **Mechanism analysis**

X-ray photoelectron spectroscopy (XPS)



UV-vis spectroscopy

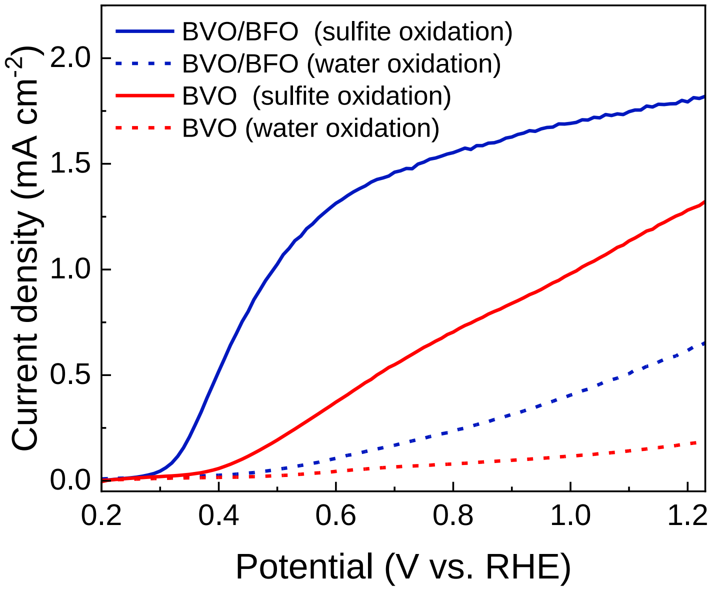


☑ **Surface modification (abundant oxygen vacancies)** and **photo-absorption ability** may not be the primary reason for the 3.5 times increase in photocurrent density.

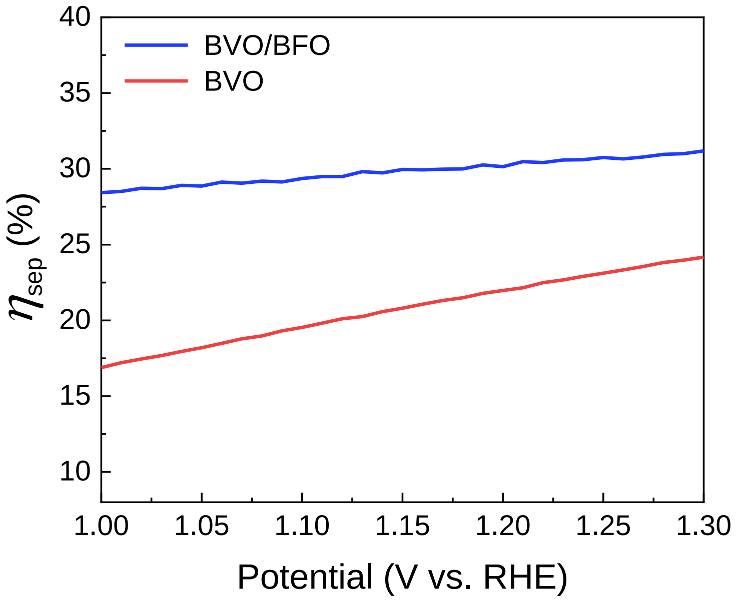
Results

❖ **Mechanism analysis**

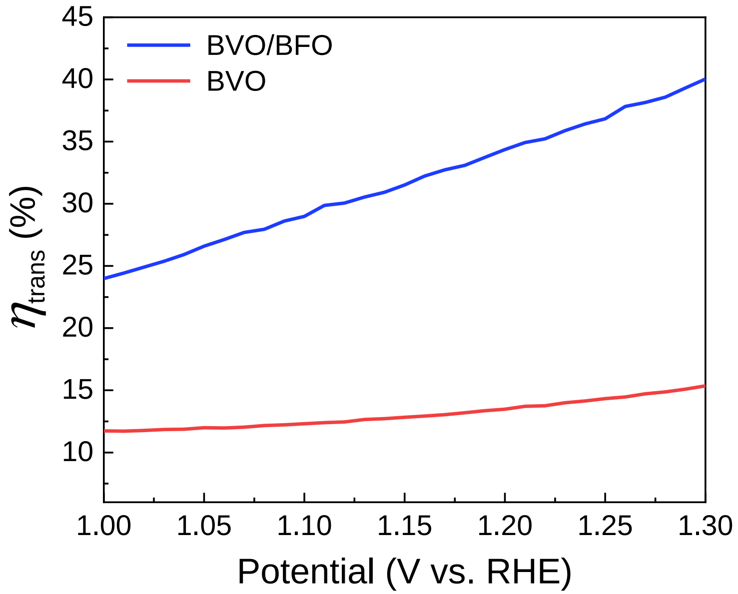
Sulfate oxidation



Charge separation efficiency



Charge transfer efficiency



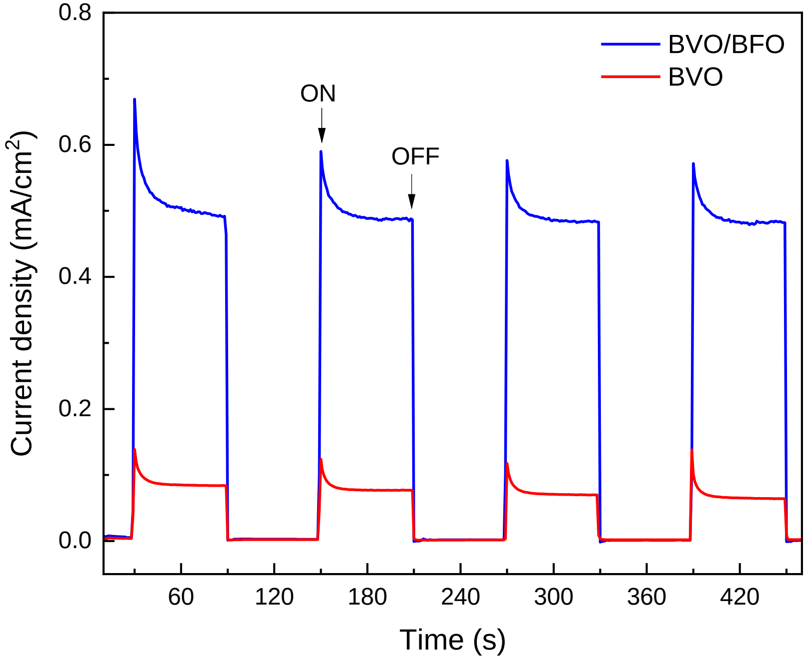
The inserted BFO thin film not only suppressed the recombination rate and promoted the reaction kinetics.

(within the BVO layer) **(at the bulk-electrolyte interface)**

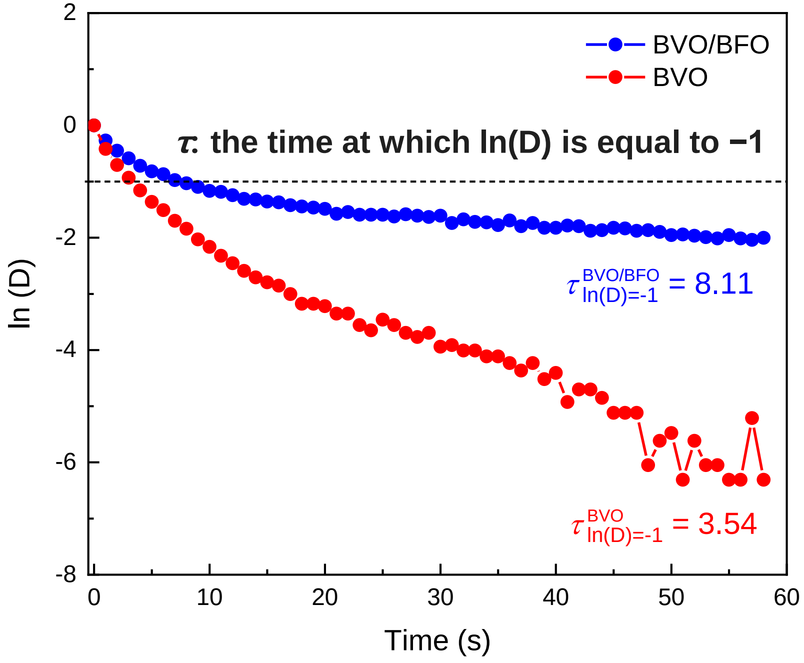
Results

❖ **Mechanism analysis**

Transient photocurrent spectra



Charge carrier lifetime



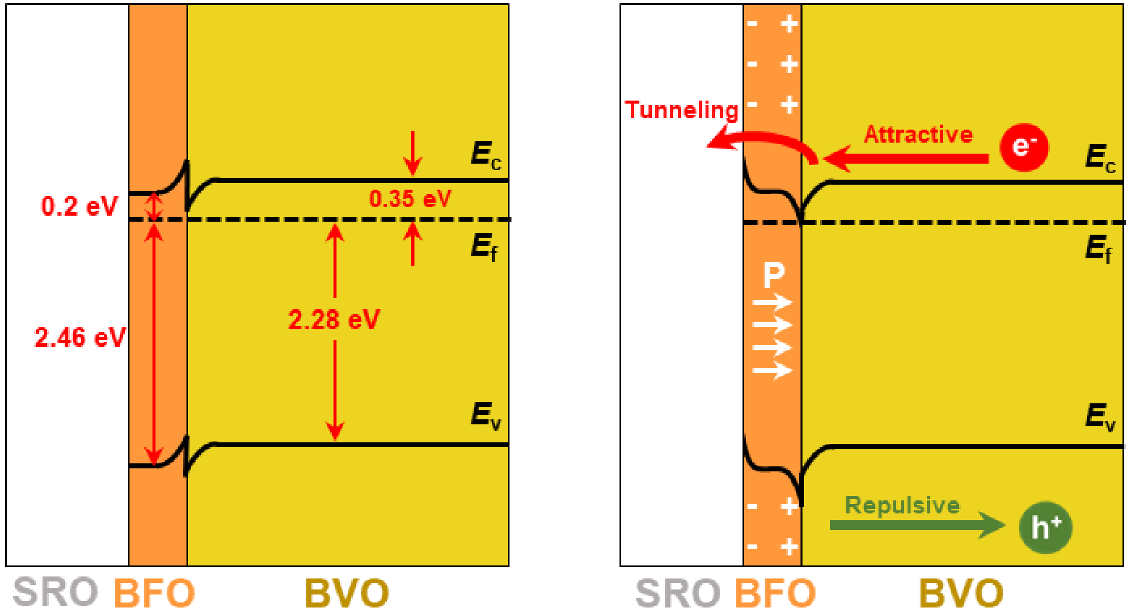
The BVO/BFO photoanode showed a longer lifetime of the electron-hole pairs than the BVO photoanode.

Better charge transport and recombination kinetics as the BFO layer is inserted

Results

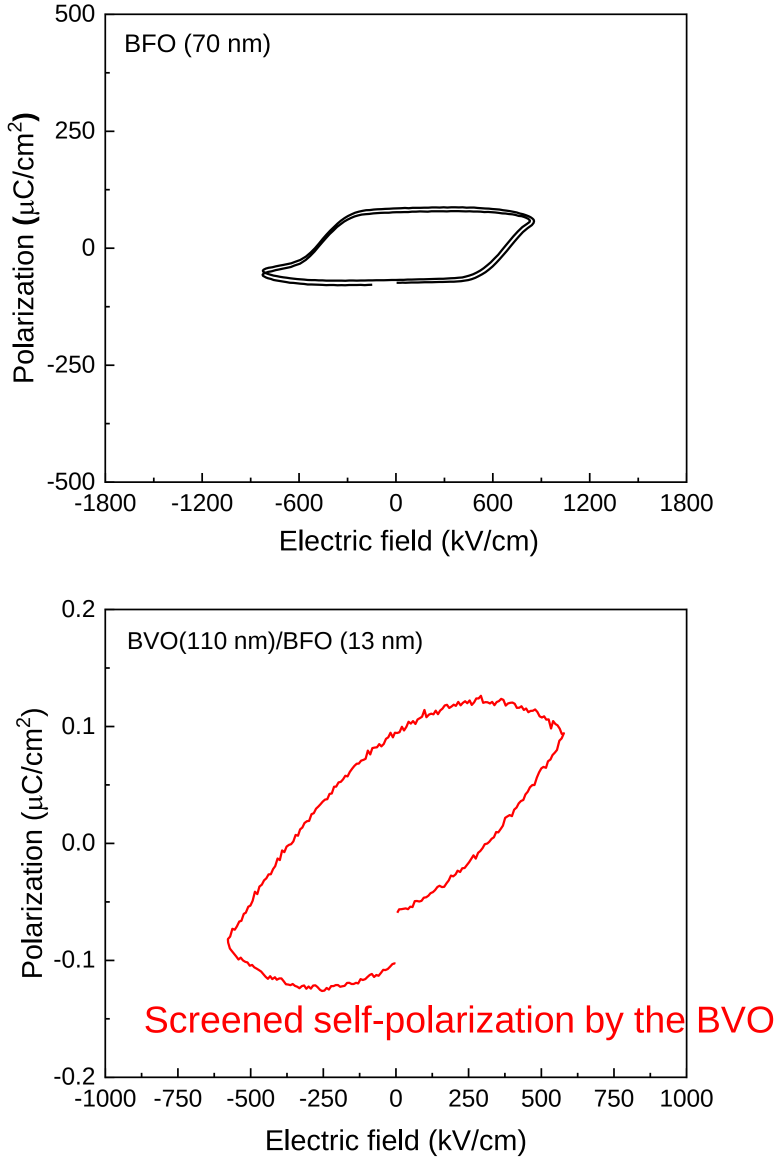
❖ Mechanism analysis

Energy band diagram

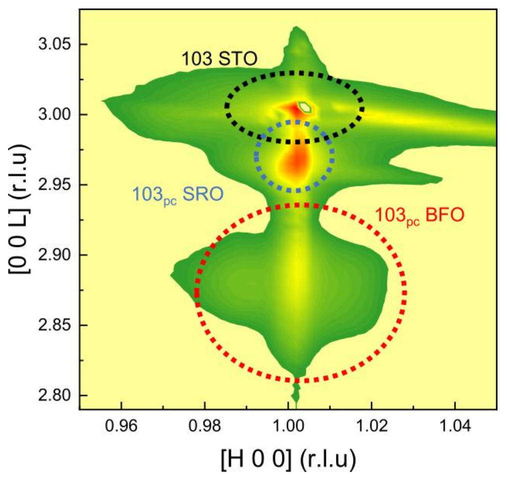


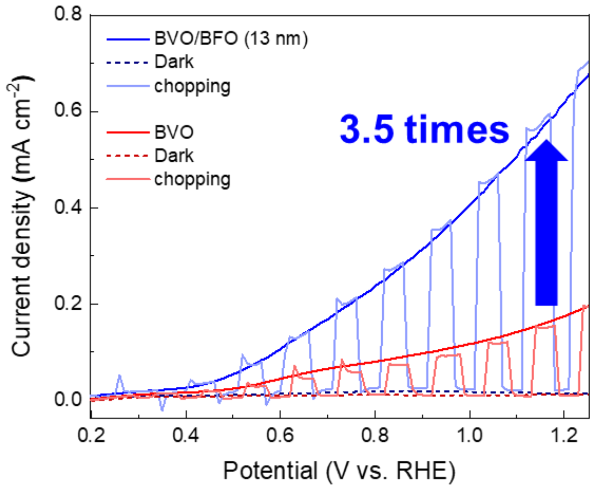
- The BFO thin film induces a strong upward self-polarization
- Holes and electrons drift in opposite directions
  → Recombination is reduced, and **the separation efficiency ↑**
  Hole repulsed to electrode/electrolyte interface,
  and **the transfer efficiency ↑**

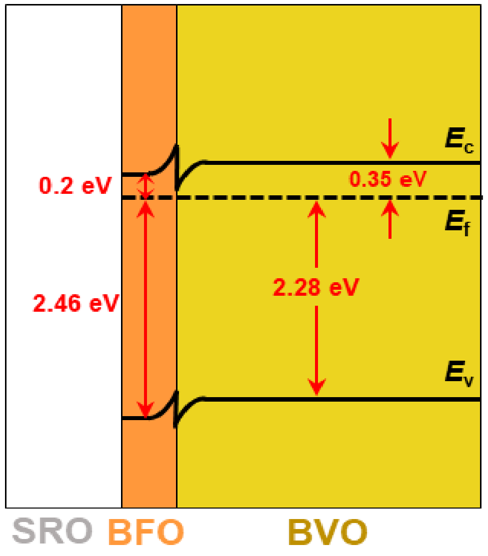
Polarization-electric (P-E) hysteresis loop

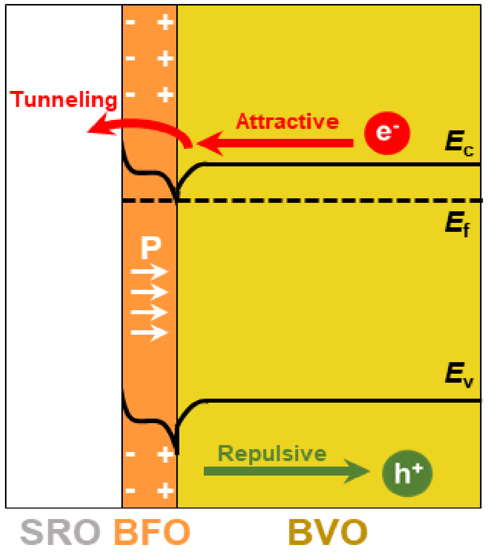


Summary









Epitaxial grown BFO thin films exhibit a strong self-polarization under the BVO layer

The photoexcited hole and electron drift in opposite directions corresponding on the self-polarization of the BFO

The BVO/BFO photoanodes show **the enhanced charge separation and transfer efficiencies** than the bare BVO photoanodes

The BVO/BFO photoanodes show 3.5 times higher photocurrent density than the BVO photoanodes

Acknowledgments

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Collaborators

Prof. Sanghan Lee (Corresponding author)

Yejoon Kim, Haejin Jang,

Hojoong Choi, Jiwoong Yang, Yoonsung Jung,

Donghyeon Lee

Prof. Ho Won Jang

Sungkyun Choi

Funding

- Future Hydrogen Original Technology Development (2021M3I3A1084747), through the National Research Foundation of Korea (NRF) funded by the Korean government. (Ministry of Science and ICT(MSIT))
- NRF grant funded by the Korea government(MSIT) (No. 2020R1A2C1005590).
- GIST Christian Research Crew (GCRC)

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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Enhancing $BiVO_4$ photoanode performance by insertion of an epitaxial $BiFeO_3$ ferroelectric layer

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ARTICLE INFO

Article history:
Received 15 September 2023
Revised 12 October 2023
Accepted 16 October 2023
Available online 7 November 2023

Keywords:
Photoelectrochemical
Photoanode
$BiVO_4$
Ferroelectric materials
$BiFeO_3$

ABSTRACT

$BiVO_4$ (BVO) is a promising material as the photoanode for use in photoelectrochemical applications. However, the high charge recombination and slow charge transfer of the BVO have been obstacles to achieving satisfactory photoelectrochemical performance. To address this, various modifications have been attempted, including the use of ferroelectric materials. Ferroelectric materials can form a permanent polarization within the layer, enhancing the separation and transport of photo-excited electron-hole pairs. In this study, we propose a novel approach by depositing an epitaxial $BiFeO_3$ (BFO) thin film underneath the BVO thin film (BVO/BFO) to harness the ferroelectric property of BFO. The self-polarization of the inserted BFO thin film simultaneously functions as a buffer layer to enhance charge transport and a hole-blocking layer to reduce charge recombination. As a result, the BVO/BFO photoanodes showed more than 3.5 times higher photocurrent density (0.65 mA cm^{-2}) at 1.23 V_{RHE} under the illumination compared to the bare BVO photoanodes (0.18 mA cm^{-2}), which is consistent with the increase of the applied bias photon-to-current conversion efficiencies (ABPE) and the result of electrochemical impedance spectroscopy (EIS) analysis. These results can be attributed to the self-polarization exhibited by the inserted BFO thin film, which promoted the charge separation and transfer efficiency of the BVO photoanodes.

Thank you for your attention

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