

# **New Metal Oxides for Efficient Hydrogen Production via Solar Water Splitting**

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2016 DOE Annual Merit Review

June 8, 2016

Project ID #

PD118

# Overview

## Timeline

- Start date: 9/2014
- Project end date: 8/2017
- Percent complete: 25%

## Budget

- Total project funding  
\$740,000
- Funding received in FY14  
\$240,000
- Funding for FY15  
\$250,000

## Barriers

- Barriers addressed
  - Y. Materials efficiency
  - Z. Materials durability
  - AB. Materials synthesis

## Partners

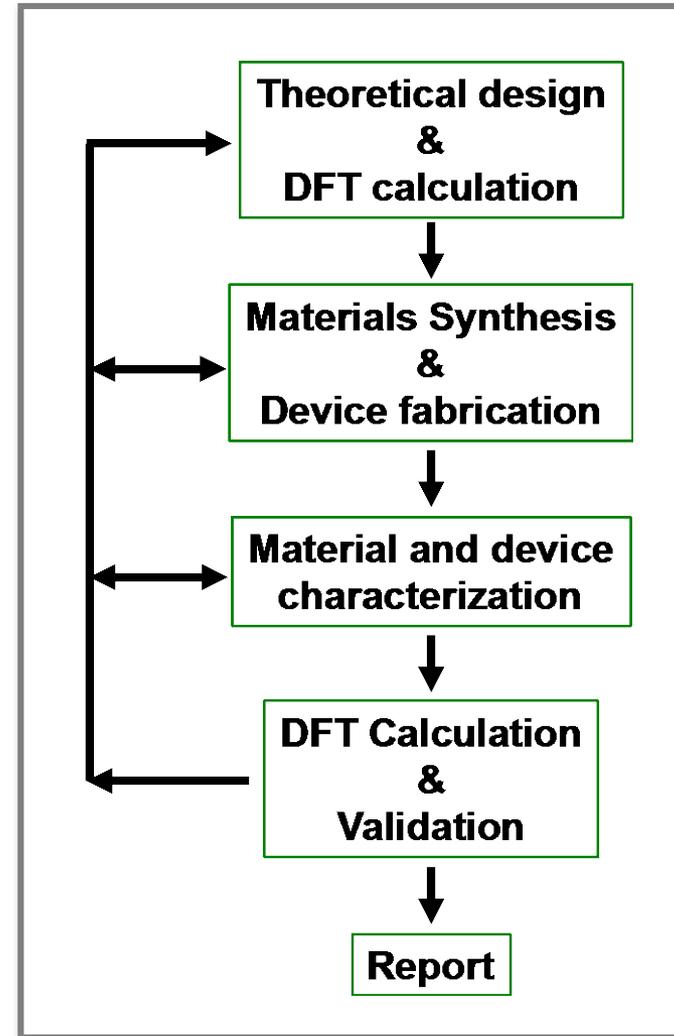
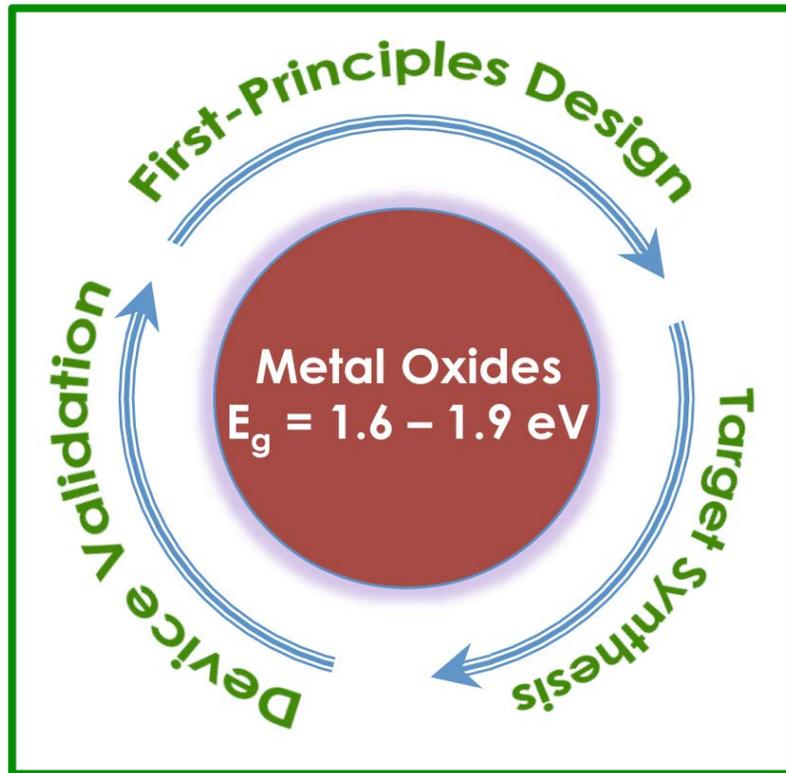
- National Renewable Energy Laboratory

# Relevance

## Project Objectives

- Design new metal oxides for PEC hydrogen production
- Develop approaches for synthesizing designed metal oxides
- Examine PEC properties of new metal oxides
- Education and outreach

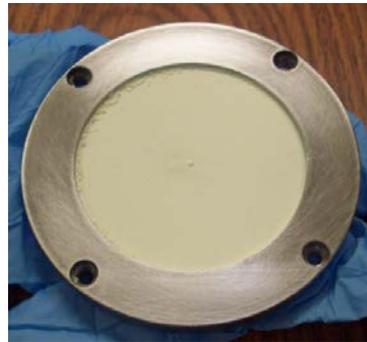
# Approach



# Accomplishments and Progress

BBNO thin films grown on FTO/glass substrate by RF sputtering

Target



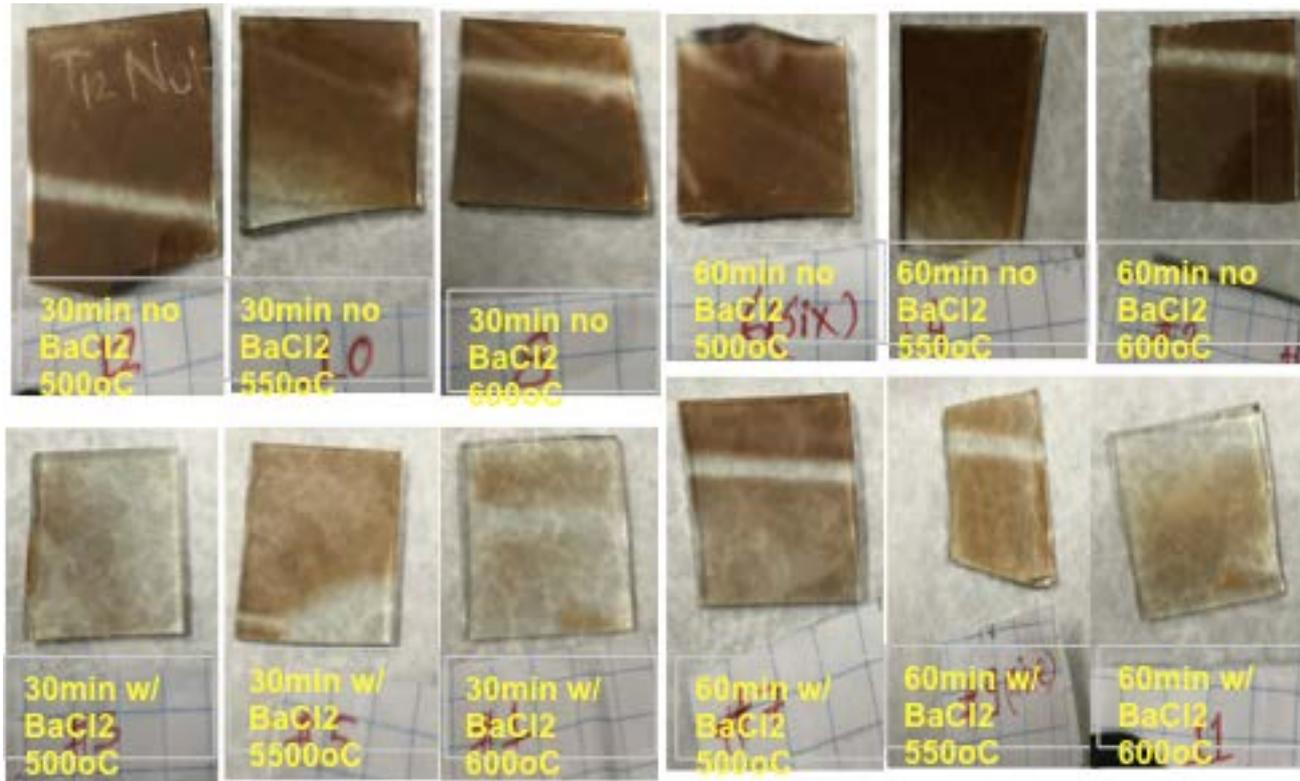
Before annealing



After annealing

# Accomplishments and Progress

BBNO thin films grown on FTO/glass substrates by RF sputtering

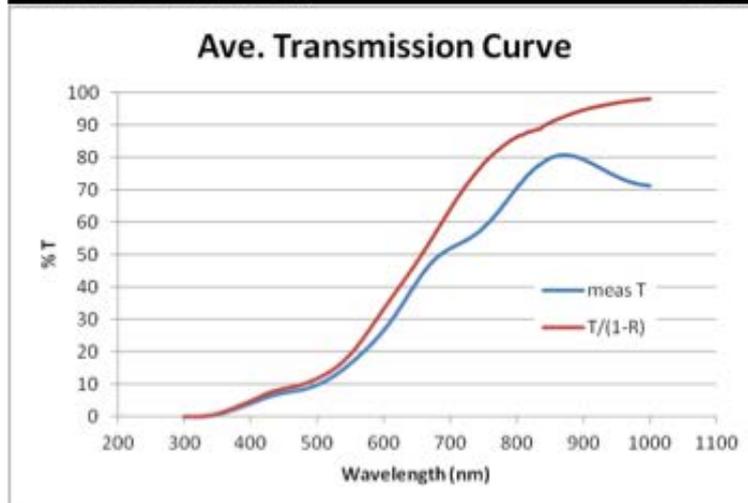
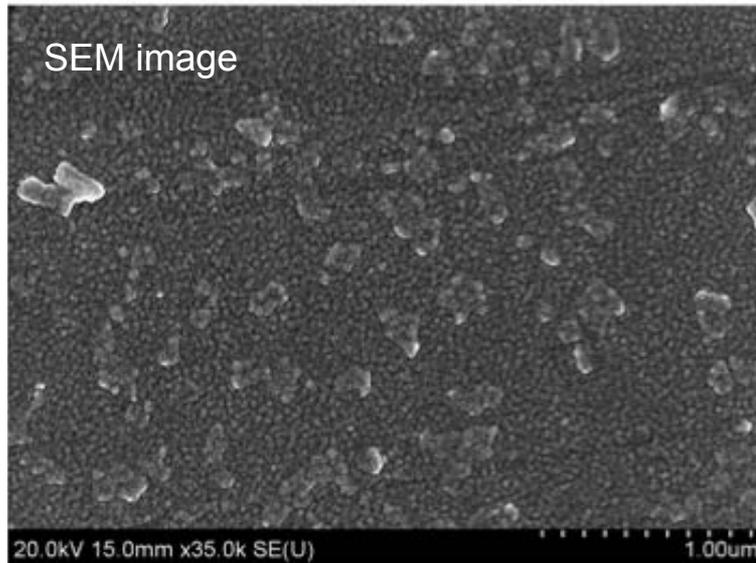


Samples w/o BaCl<sub>2</sub> appear same

Samples with BaCl<sub>2</sub> show loss of color

# Accomplishments and Progress

BBNO thin films grown on FTO/glass substrates by RF sputtering

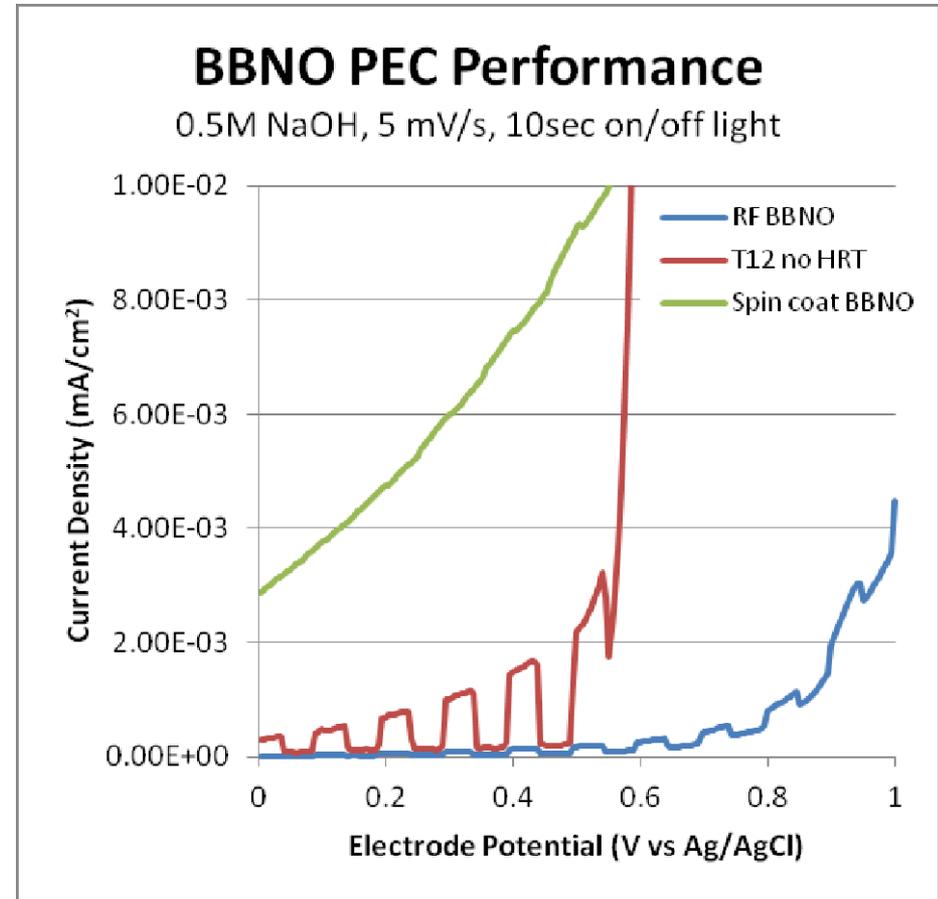


Room temp deposited  
30min 500°C air anneal  
Direct bandgap:  
Approx. 2.05 eV  
Single phase confirmed by XRD  
Rhombohedral (R-3)  
Perovskite structure  
 $R_{\text{sheet}}: \sim 1.5 \times 10^9 \Omega/\square$

# Accomplishments and Progress

BBNO thin films grown on FTO/glass substrates by RF sputtering

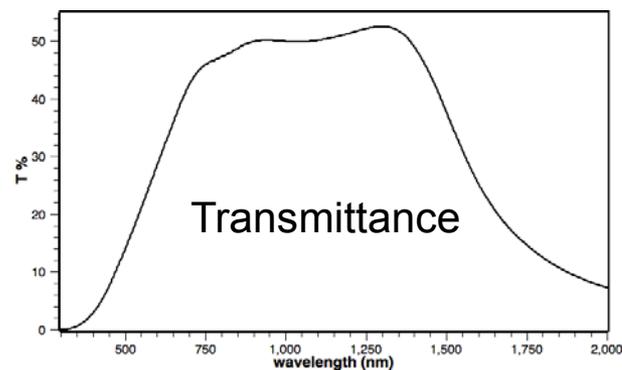
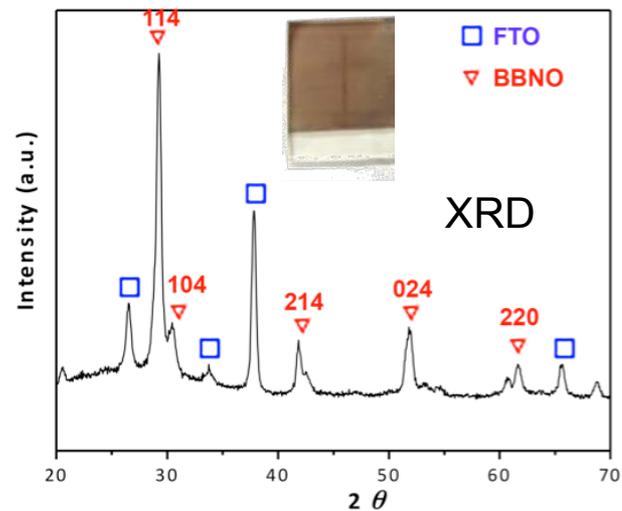
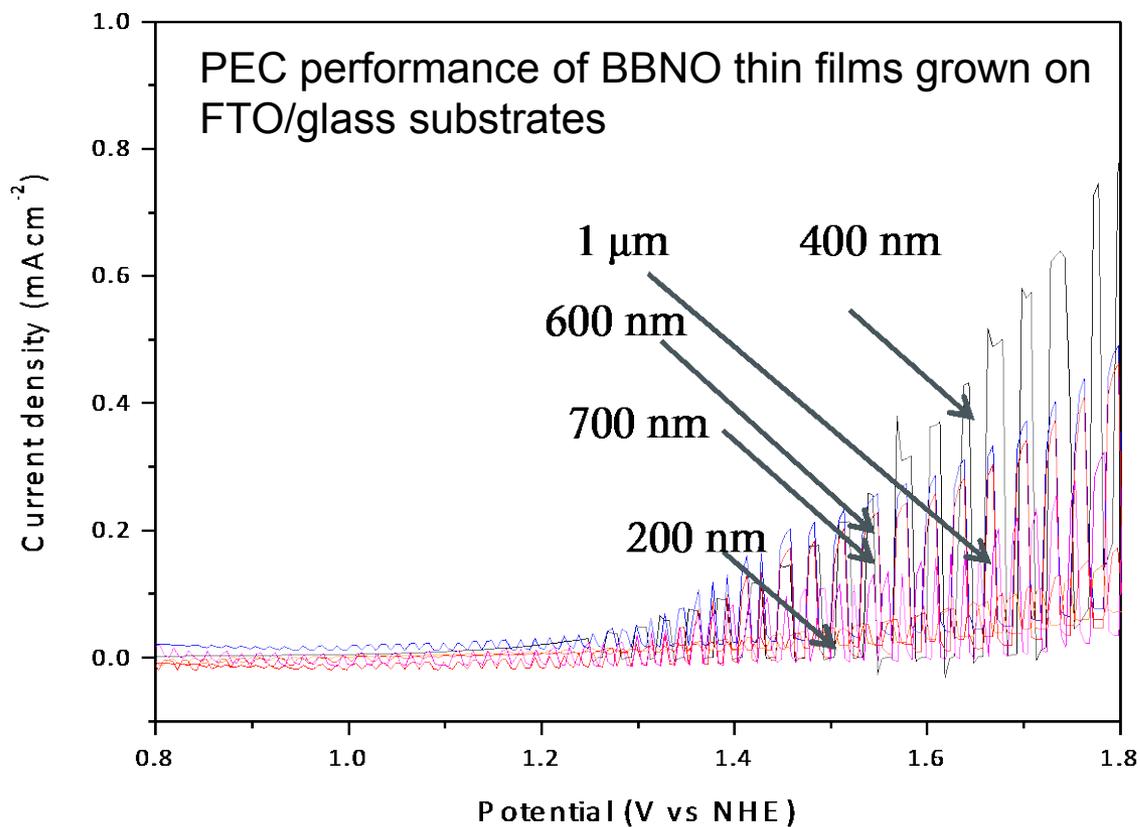
- Thin film synthesis
  - RF sputtered “Hasitha” system
  - Room temp, 240min, 50W, 10mTorr, 30 sccm Ar
  - ~ 200nm thick film
- PEC testing using 300W Xe light source
  - 1M NaOH (first, all electrodes)
  - 1M Na<sub>2</sub>SO<sub>3</sub> & 0.5M KH<sub>2</sub>PO<sub>3</sub> (referred to as “SS/PP”)



# Accomplishments and Progress

BBNO thin films on FTO/substrates grown by Sol-gel method

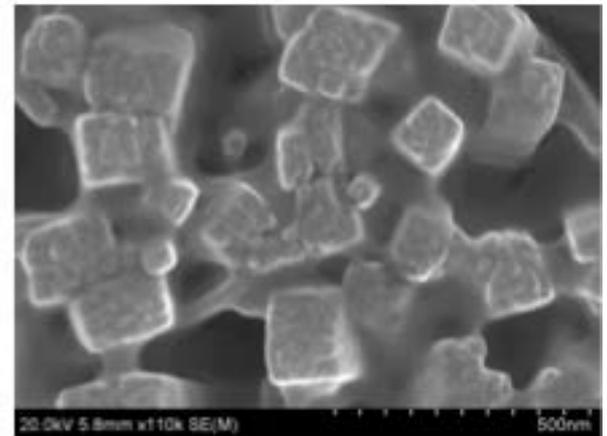
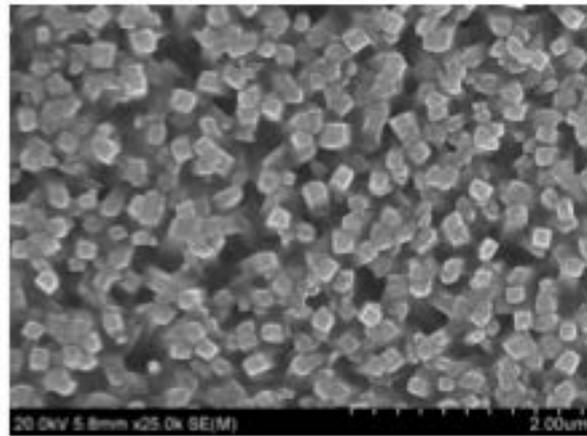
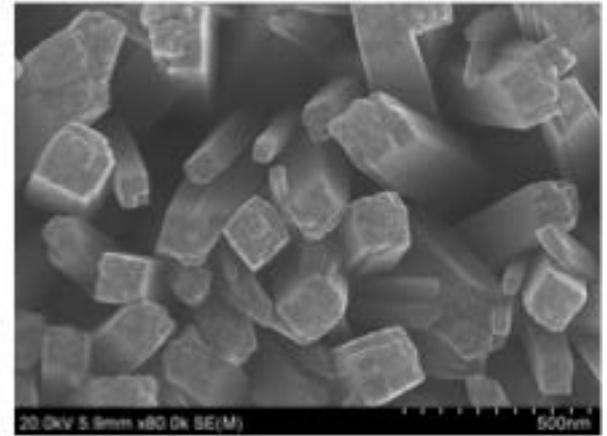
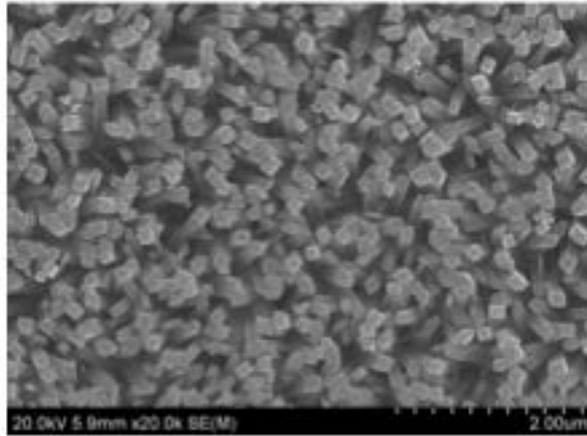
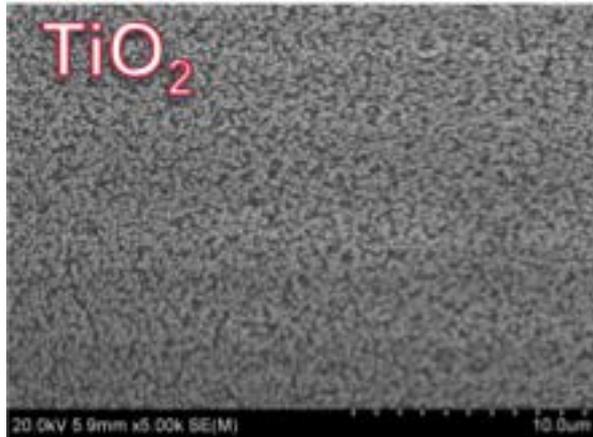
Acetylacetonate as chelating reagent  
Ethyl glycol as solution  
Spin-coating



# Accomplishments and Progress

BBNO thin films grown on  $\text{TiO}_2$  nanowire arrays

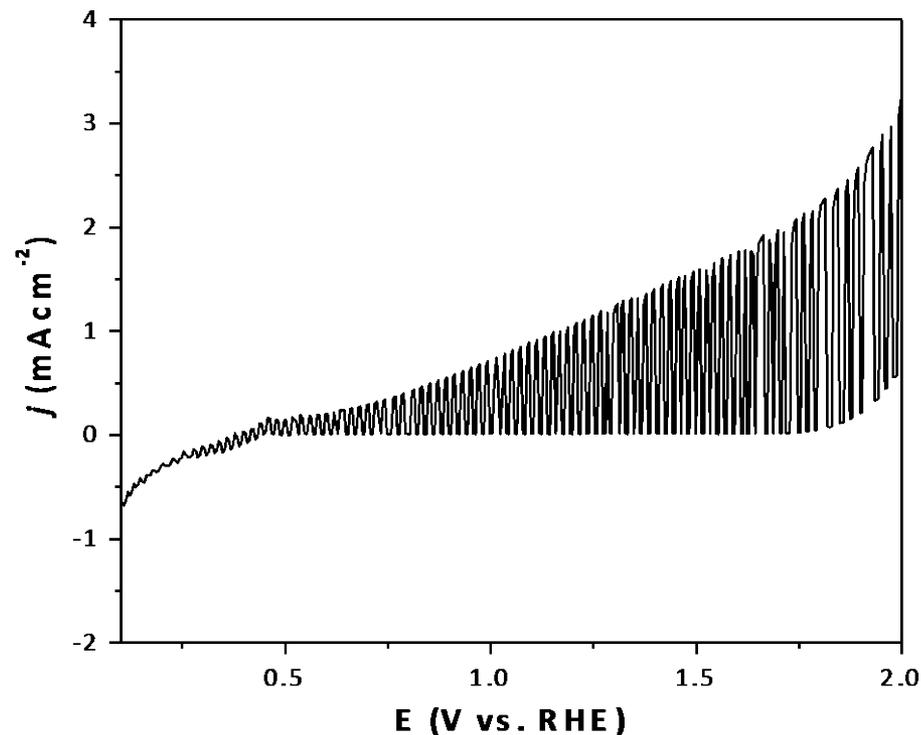
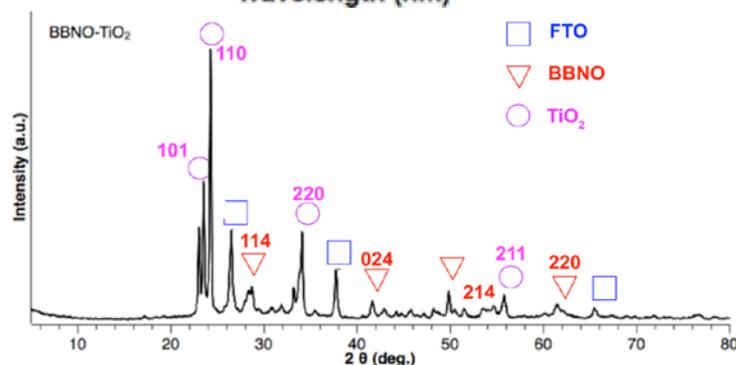
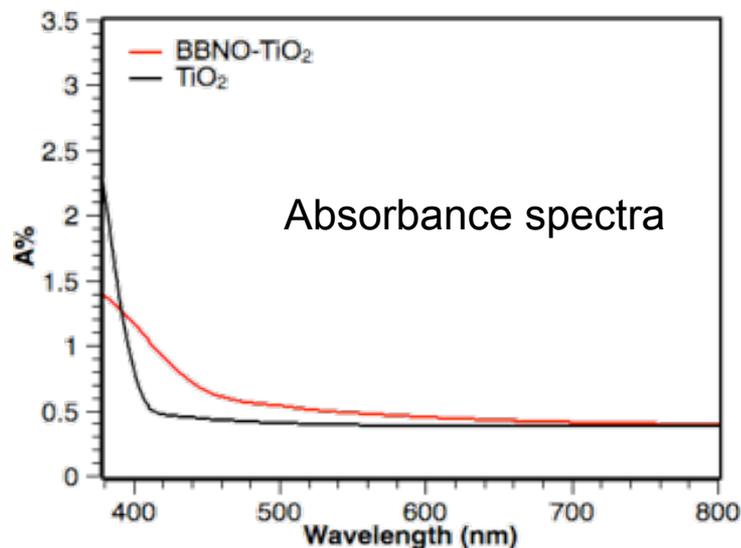
1) band position engineering; 2) high surface areas; 3) promote charge transfer



# Accomplishments and Progress

BBNO thin films grown on TiO<sub>2</sub> nanowire arrays

- Enhanced light absorption by TiO<sub>2</sub> nanowire arrays
- Improved PEC performance



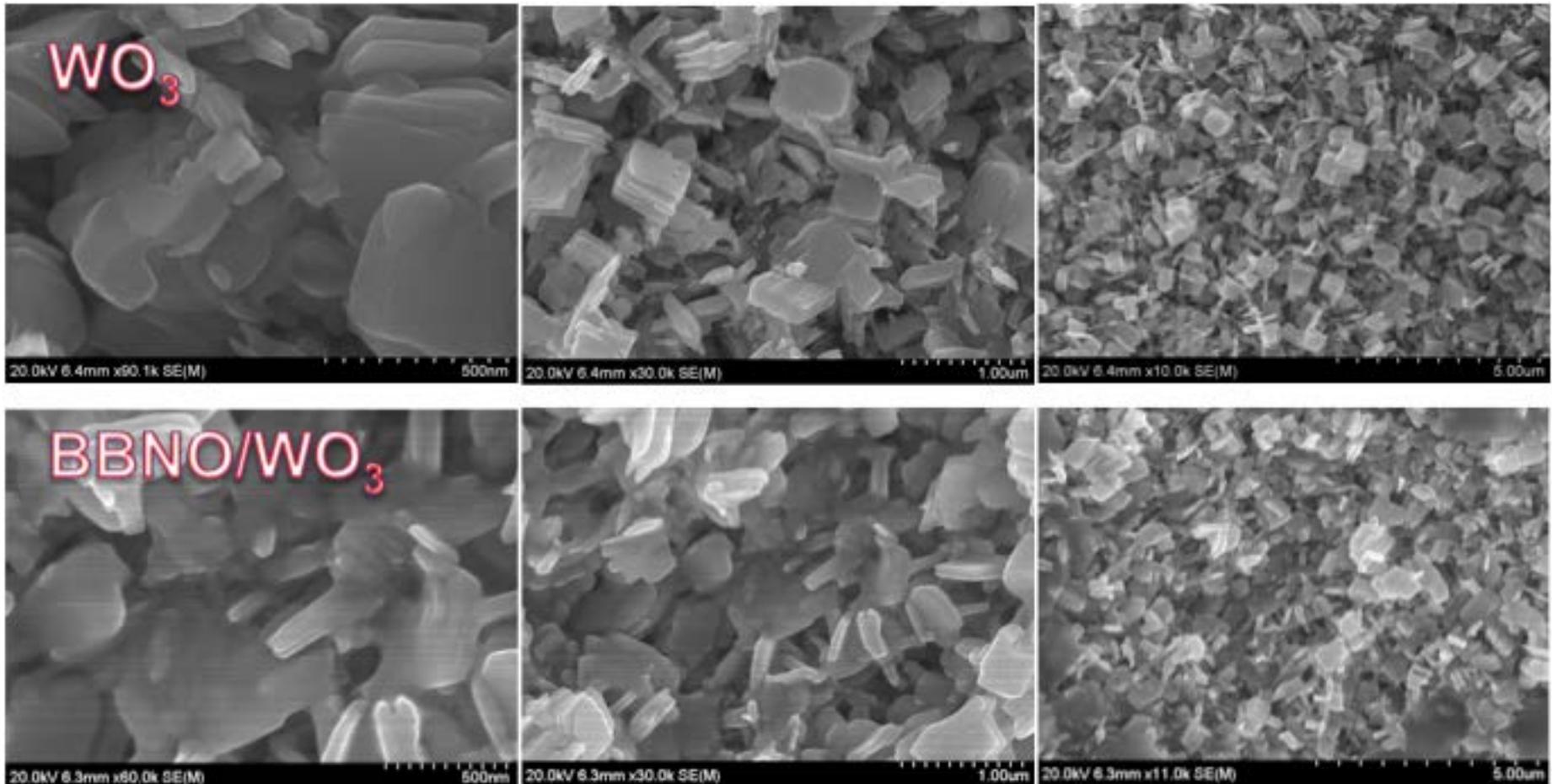
PEC performance of BBNO grown on TiO<sub>2</sub> nanowire arrays

XRD curve of BBNO grown on TiO<sub>2</sub> nanowire arrays

# Accomplishments and Progress

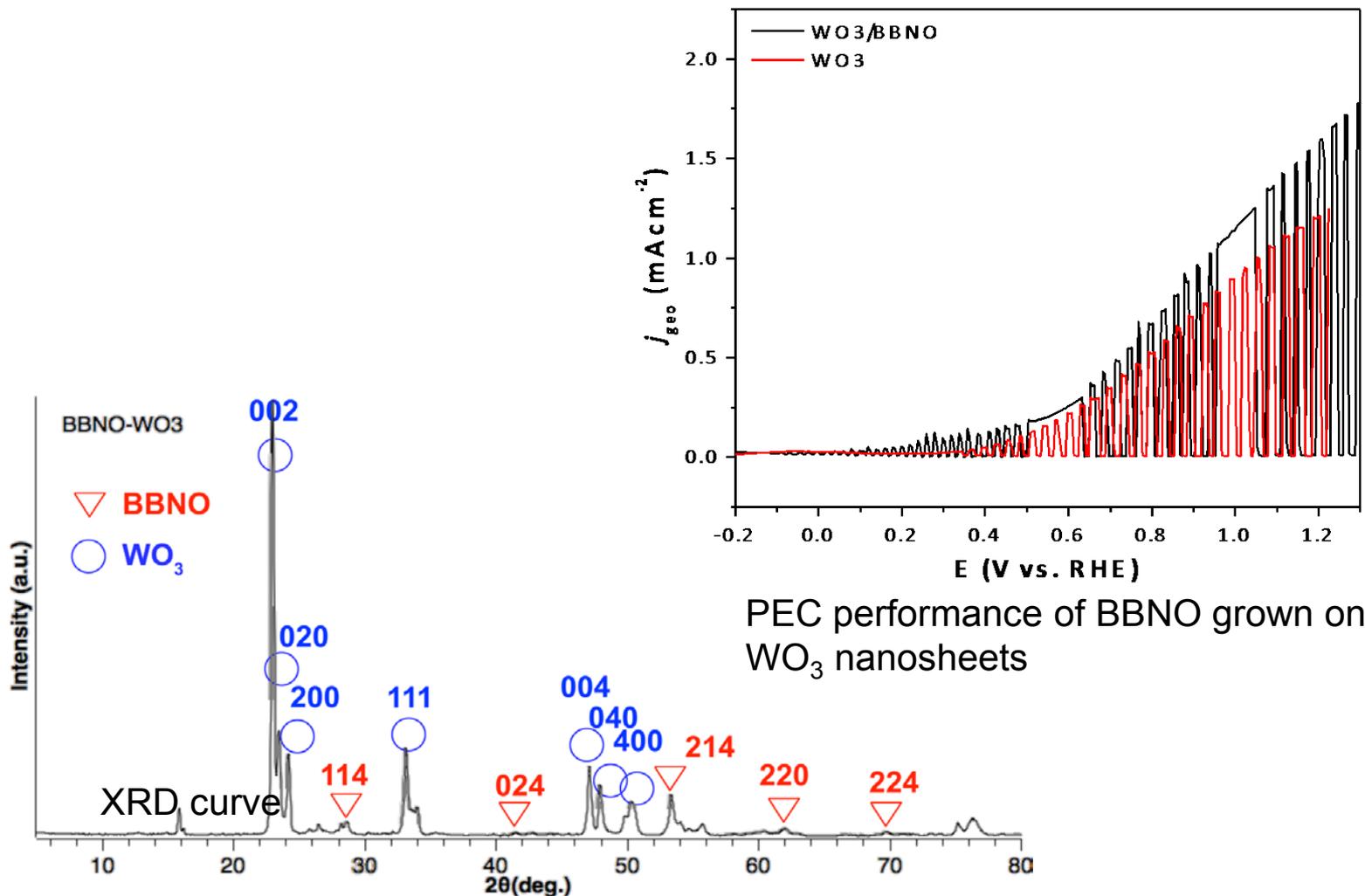
BBNO thin films grown on  $\text{WO}_3$  nanosheets

1) 2-D materials; 2) band position engineering- lower conductive band



# Accomplishments and Progress

BBNO thin films grown on  $\text{WO}_3$  nanosheets



PEC performance of BBNO grown on  $\text{WO}_3$  nanosheets

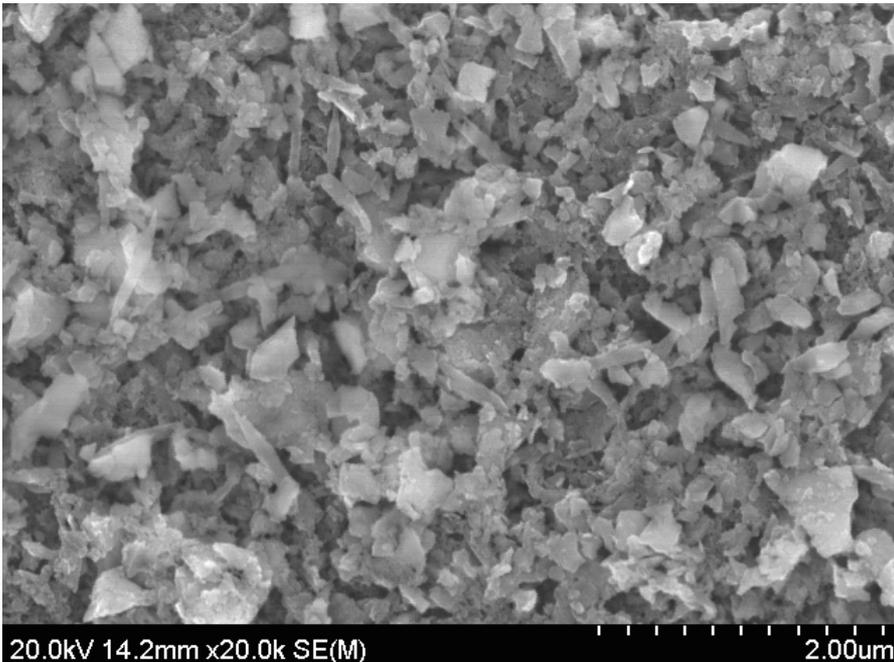
XRD curve of BBNO grown on  $\text{WO}_3$  nanosheets

# Accomplishments and Progress

## BBNO nanopowders

BBNO size reduction:

- 1) Enhance surface areas to improve electrolyte contact
- 2) Exploring the facet orientation effects
- 3) Photocatalytic water splitting using both conductive and valence bands



# Accomplishments and Progress

## BBNO nanopowders

Ball milled for total 11.5 hours

300 rpm

20-30mL acetone

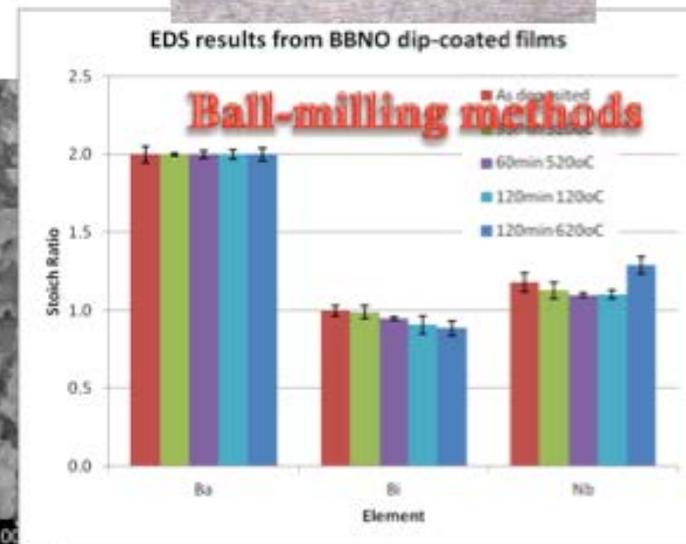
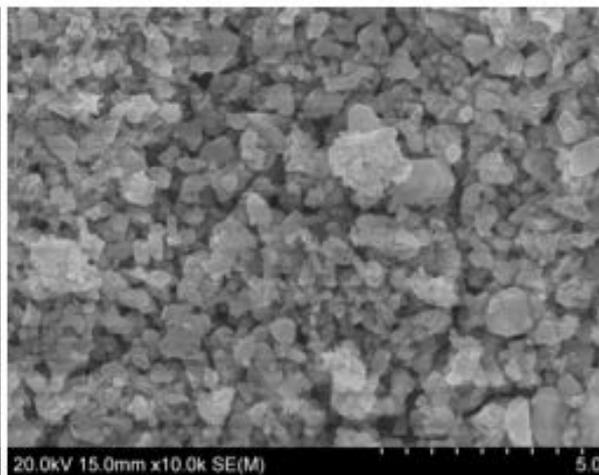
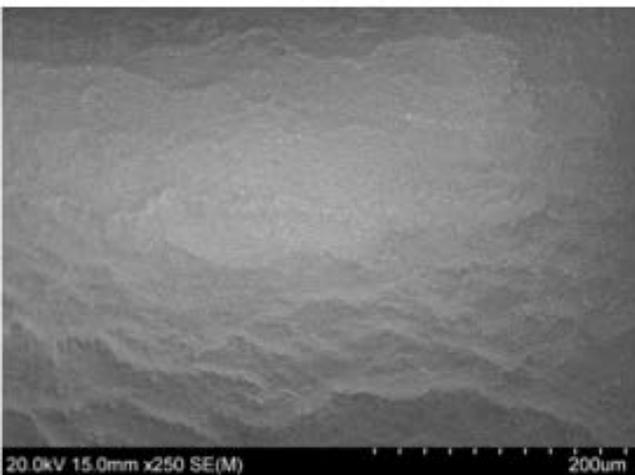
Agate jar & balls

100x 6mm diameter

16x 10mm diameter

Reversed directions (CW, CCW) every few hours

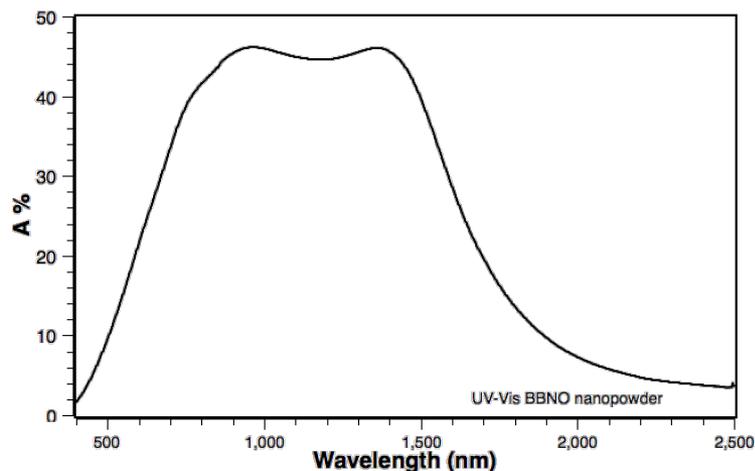
Diluted final suspension to ~60mL with acetone



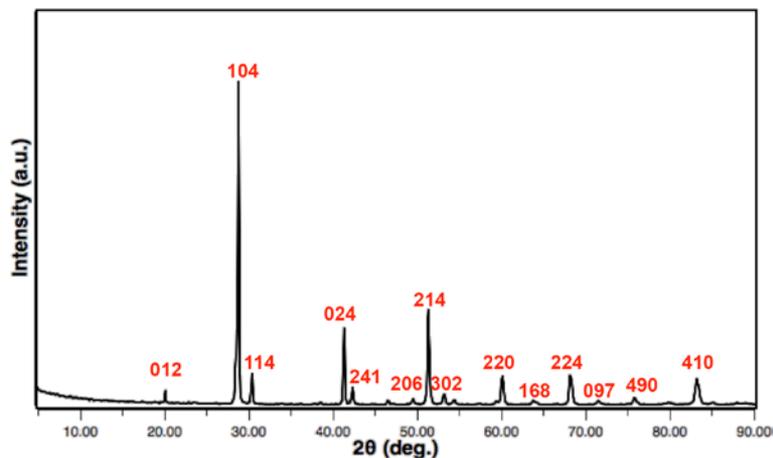
- Film surface mostly smooth with visible “wrinkles” – not cracks 15

# Accomplishments and Progress

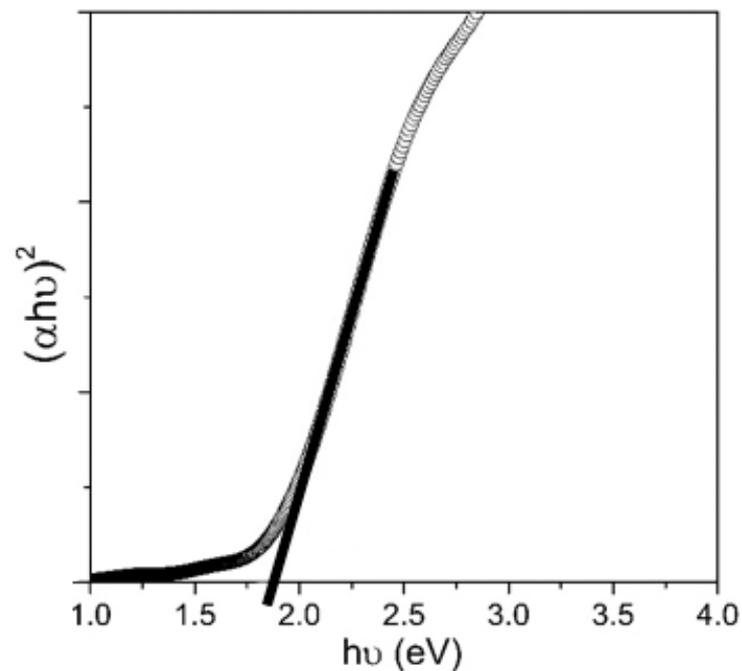
## BBNO nanopowders



Absorbance of a BBNO nanopowder film



XRD curve of a BBNO nanopowder film



Absorbance of a BBNO nanopowder film

Well crystallized double perovskite structure, Band-gap: 1.8 eV

# **Reviewers Comments**

**N/A**

# **Collaborations**

**Todd Deutsch  
National Renewable Energy Laboratory**

# Remaining Challenges

- BBNO thin films are too resistive.
- Charge transfer is not efficient
- Photocurrents are not high

# Proposed Future Work

- Continue to explore nanostructures to facilitate charge transfer.
- Apply catalysts for oxygen evolution reaction
- Test slurry configurations
- Try to dope BBNO thin films.

# Technology Transfer Activities

- N/A

# Summary

- BBNO thin films were deposited on 1D TiO<sub>2</sub> nanowires and WO<sub>3</sub> nanosheets to improve photocurrents.
- BBNO nanoparticles were prepared.
- The optical properties of BBNO prepared by RF sputtering and spin-coating methods were studied