New Metal Oxides for Efficient Hydrogen Production via Solar Water Splitting

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2017 DOE Annual Merit Review

June 7, 2017

Project ID # PD118

Overview

Timeline

- Start date: 9/2014
- Project end date: 8/2017
- Percent complete: 75%

Budget

- Total project funding $740,000
- Funding received in FY14 $140,000
- Funding received FY15 $200,000
- Funding received FY16 $200,000

Barriers

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

Partners

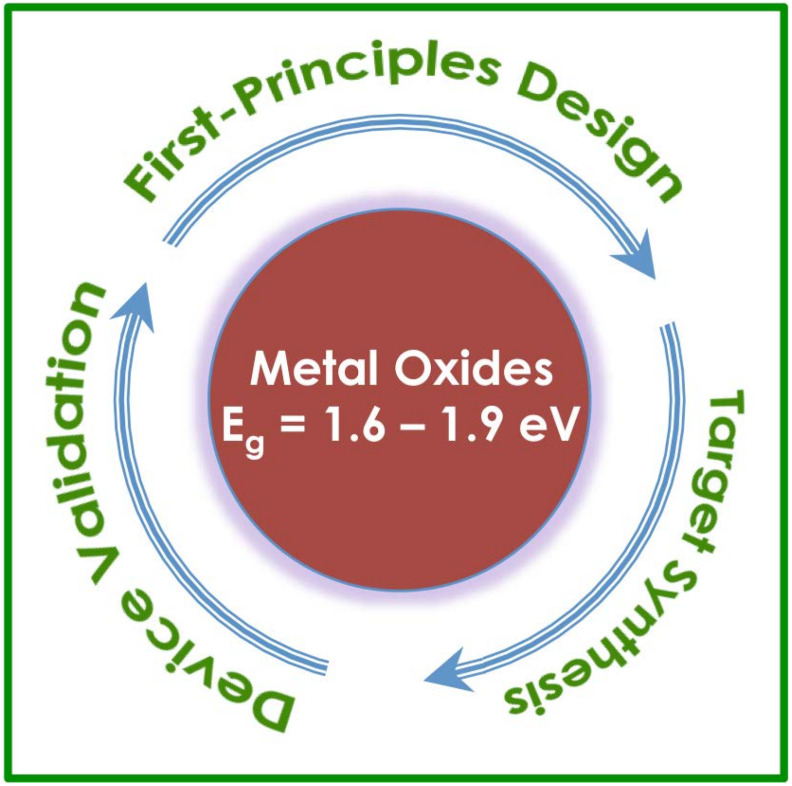
- National Renewable Energy Laboratory

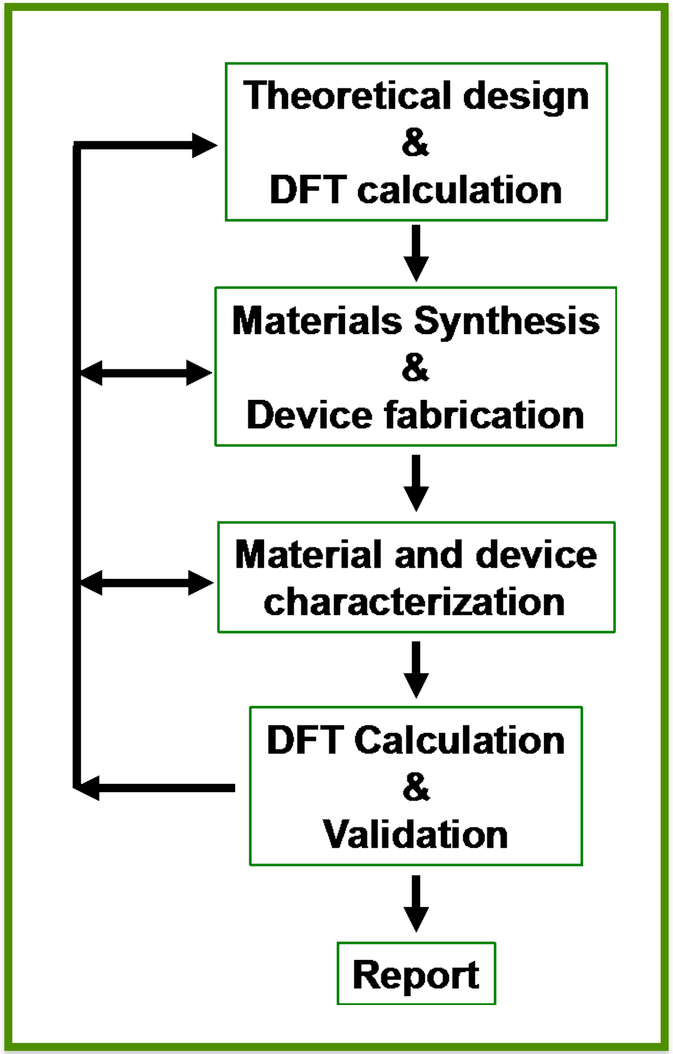
Relevance

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

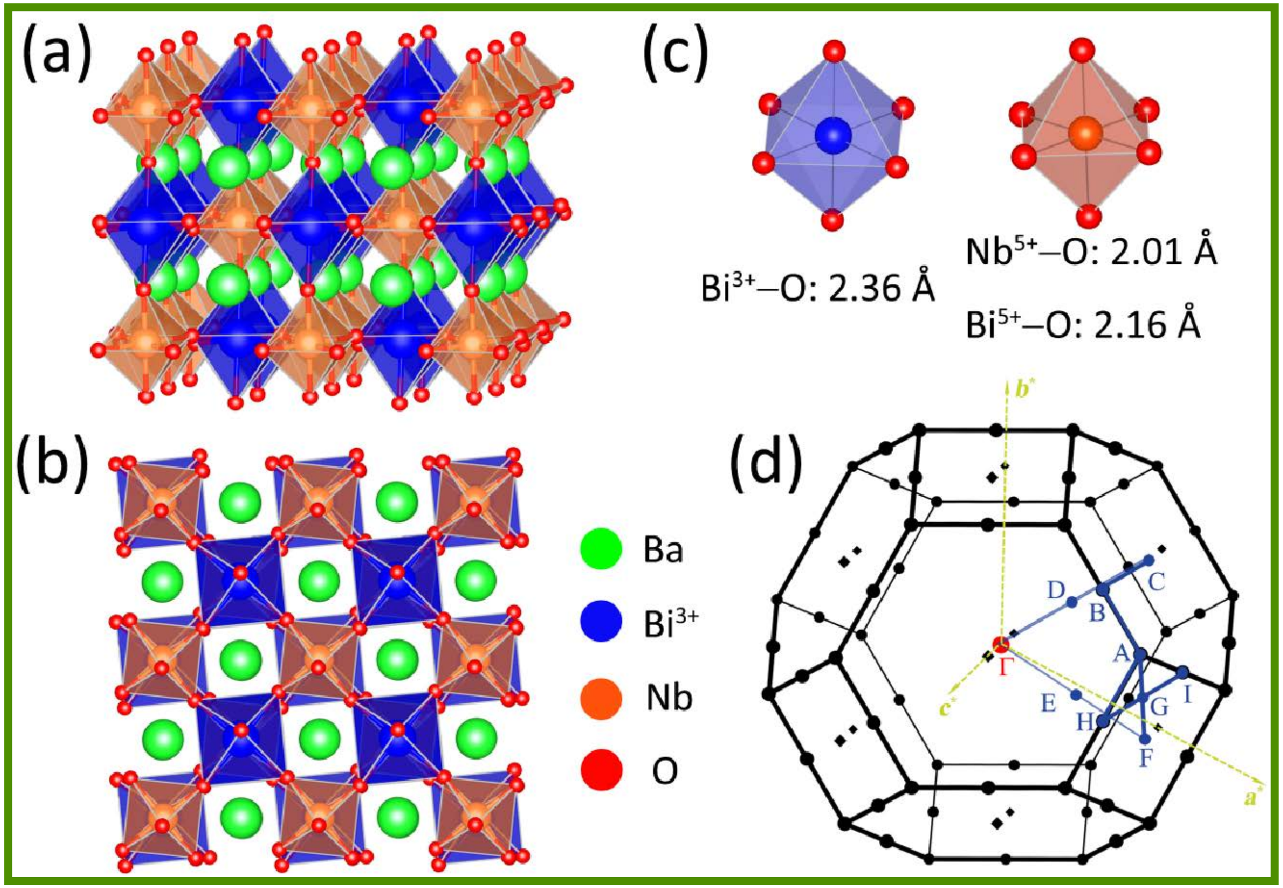




Iterative theory guidance, material synthesis, device validation

Accomplishments and Progress

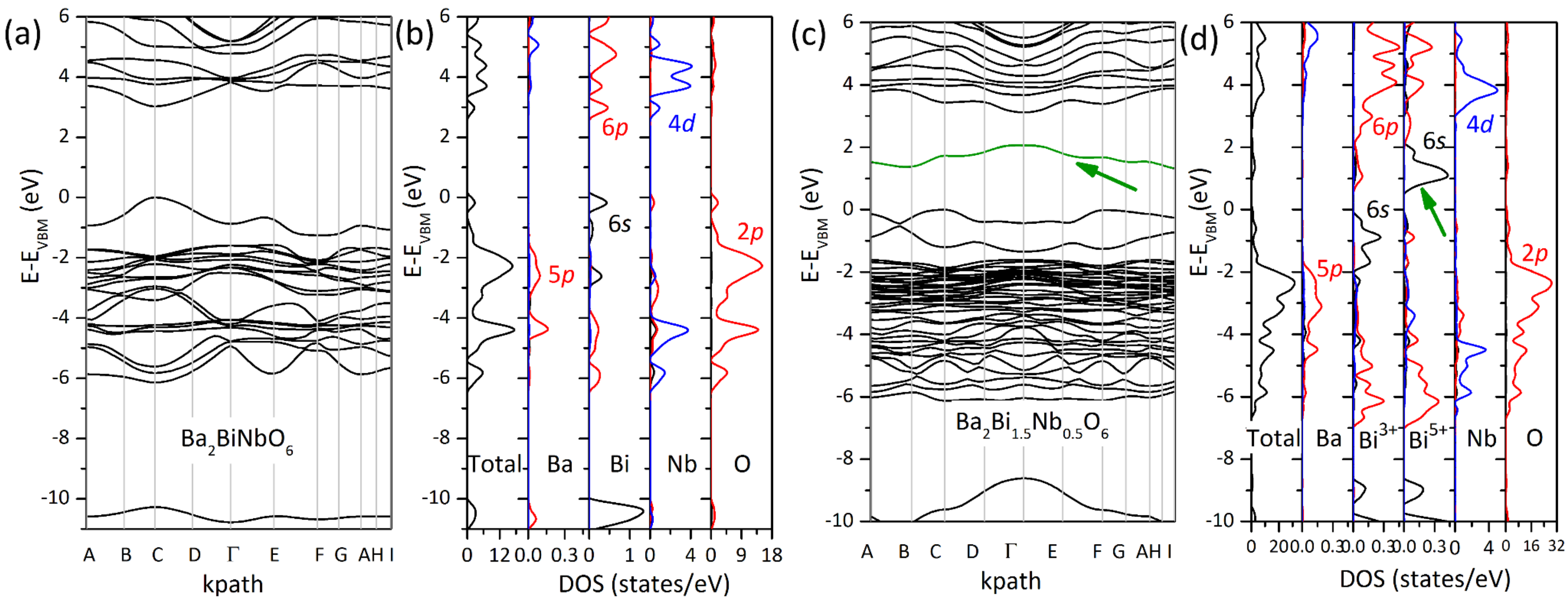
A new approach was proposed to engineer the bandgap of barium bismuth niobate (BBNO) double perovskite by DFT calculations



Crystal structure of $Ba_2Bi(Bi_x/Nb_{1-x})O_6$ along (a) [100] direction and (b) [111] direction. (c) Octahedral for $[Bi^{3+}O_6]$ and $[(Bi^{5+}/Nb^{5+})O_6]$ and their bond lengths. (d) Primary Brillouin zone in reciprocal space. *k-lines* for band structure calculation are colored in blue.

Accomplishments and Progress

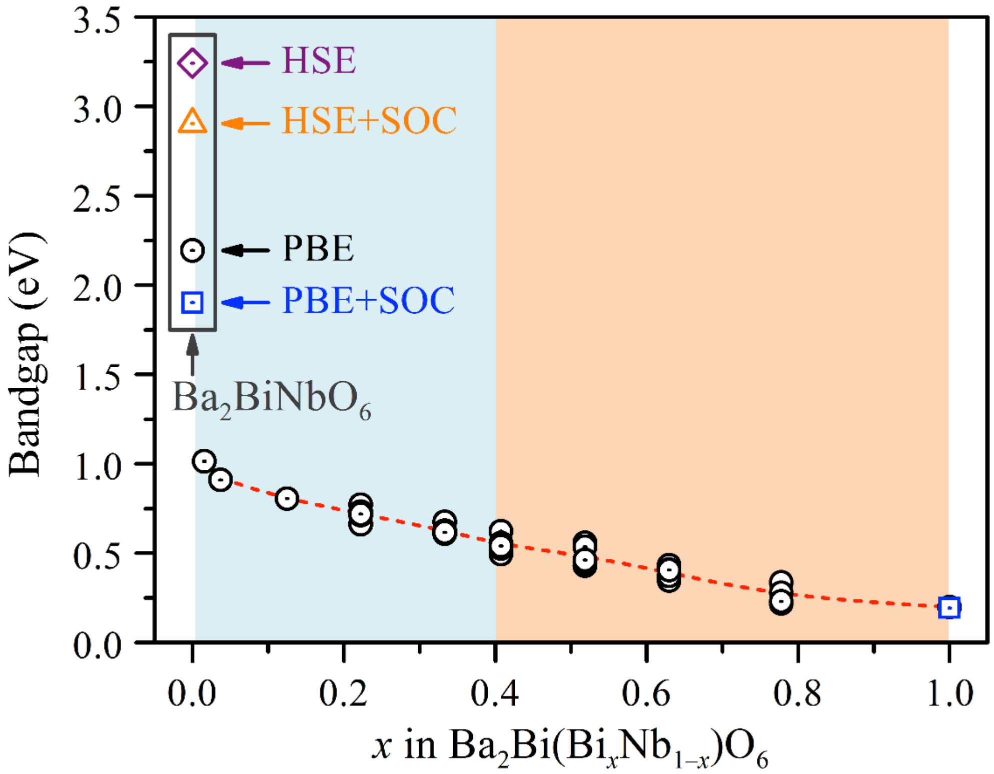
A new approach was proposed to engineer the bandgap of BBNO double perovskite by DFT calculations



(a), (c) Band structures and (b), (d) total and partial DOS of Ba_2BiNbO_6 and $Ba_2Bi_{1.5}Nb_{0.5}O_6$.

Accomplishments and Progress

A new approach was proposed to engineer the bandgap of BBNO double perovskite by DFT calculations



PBE calculated bandgap energies of $Ba_2Bi_{1+x}Nb_{1-x}O_6$ as a function of x. For comparison, the HSE, HSE+SOC, PBE, and PBE+SOC calculated bandgaps of Ba_2BiNbO_6 were also shown.

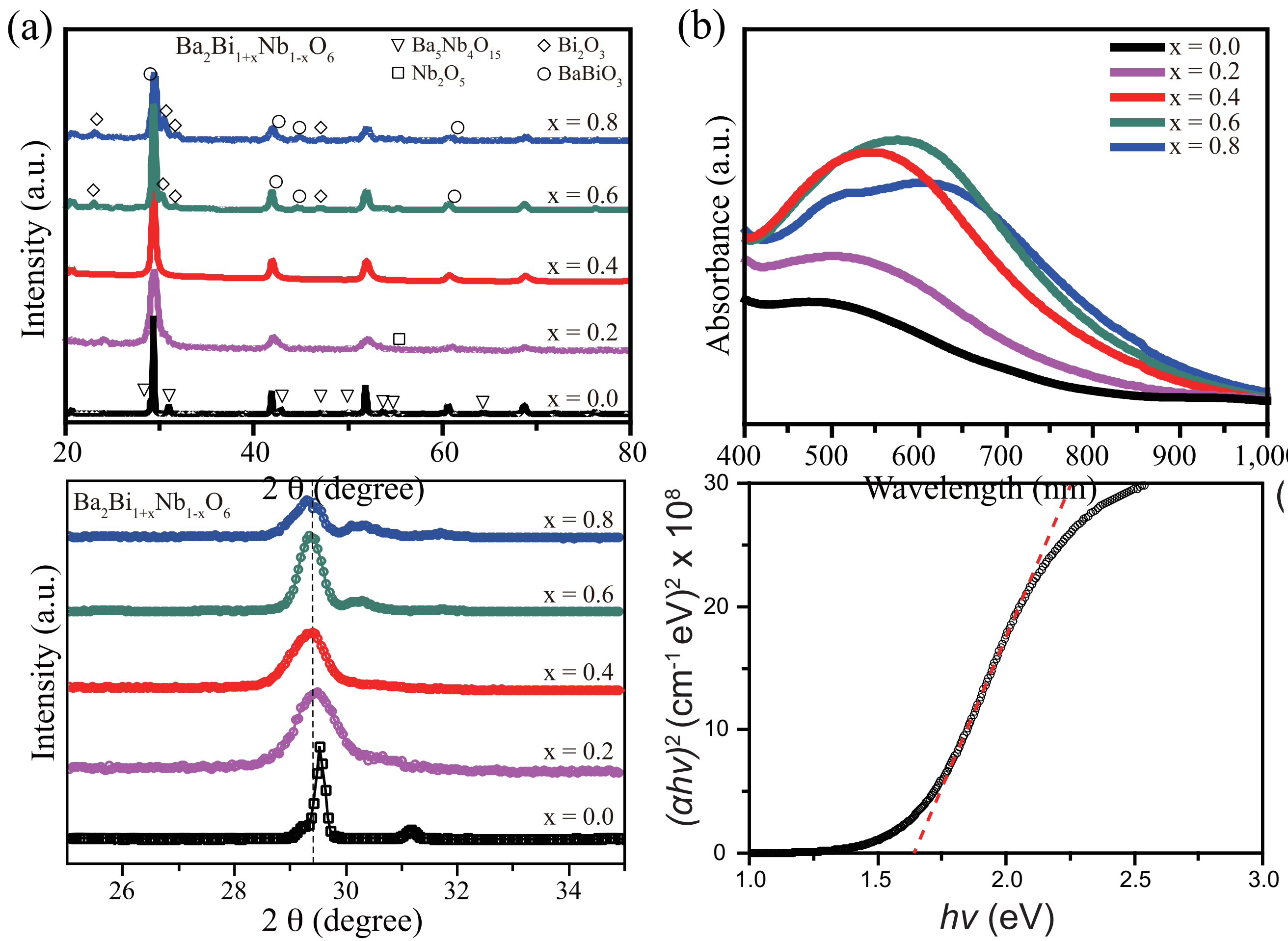
Accomplishments and Progress

The new approach was validated by experimental synthesis and characterization

- BBNO precursor solutions were prepared by (1) first dissolving Ba and Bi acetates in a mixture of acetic acid and ethylene glycol (1:1 v:v); (2) then dissolve Nb ethoxide in the solution under vigorous stirring.
- BBNO samples were prepared on FTO-coated glass substrates via spin coating of a mixed precursor solution followed by an annealing treatment.
- Co_3O_4 catalyst particles were synthesized by spin coating 1 mM $Co(NO_3)_2$ solution in acetone (using the same spin speed and time) and annealing at 500 ^{o}C for 1 h in air.

Accomplishments and Progress

The new approach was approved by experimental synthesis and characterization



Even with impurity phases, the samples show absorbance with a trend consistent with that predicted by our DFT calculations.

Accomplishments and Progress

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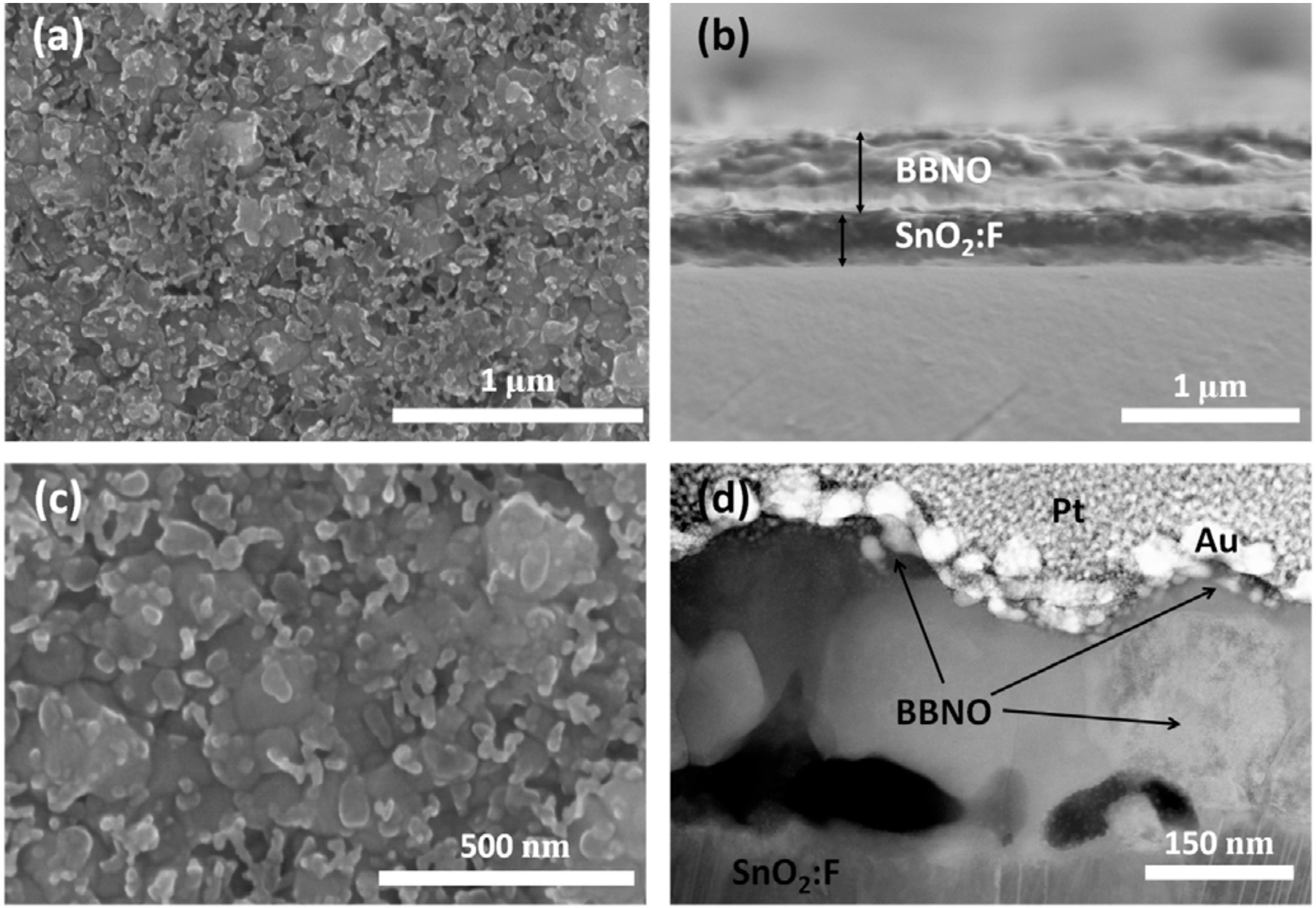

(a) Top-view SEM image of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film deposited on FTO at medium magnification (x50k). (b) Cross-section view SEM image at medium magnification (x35k). (c) Top-view SEM image at higher magnification (x100k). (d) Cross-sectional dark-field TEM image.

Accomplishments and Progress

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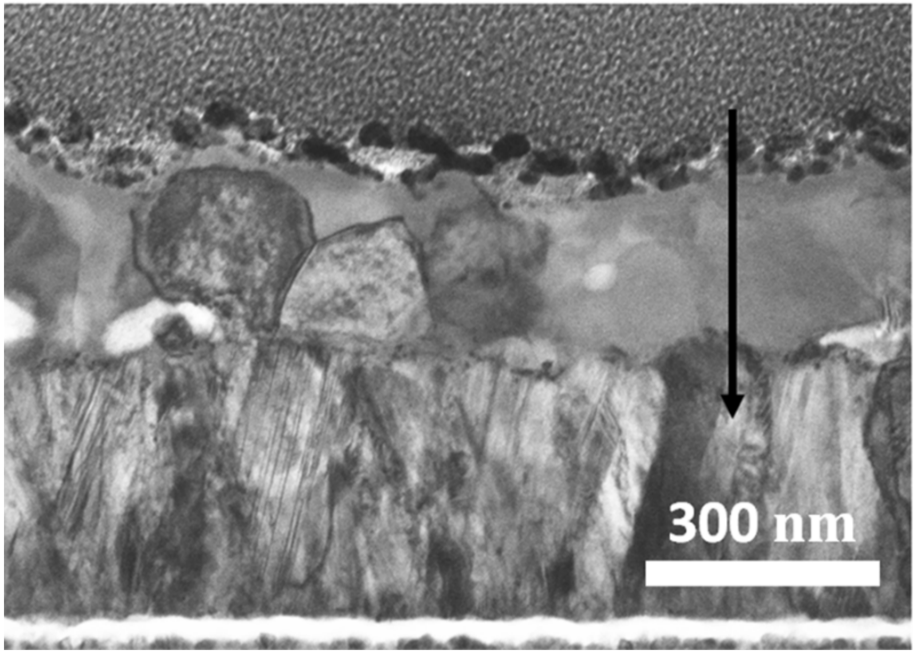
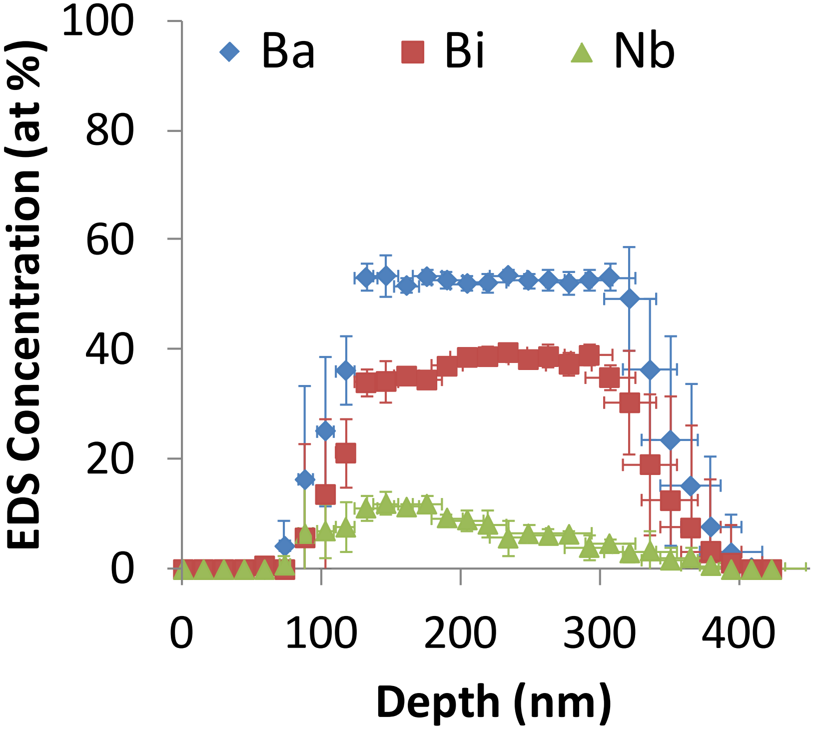
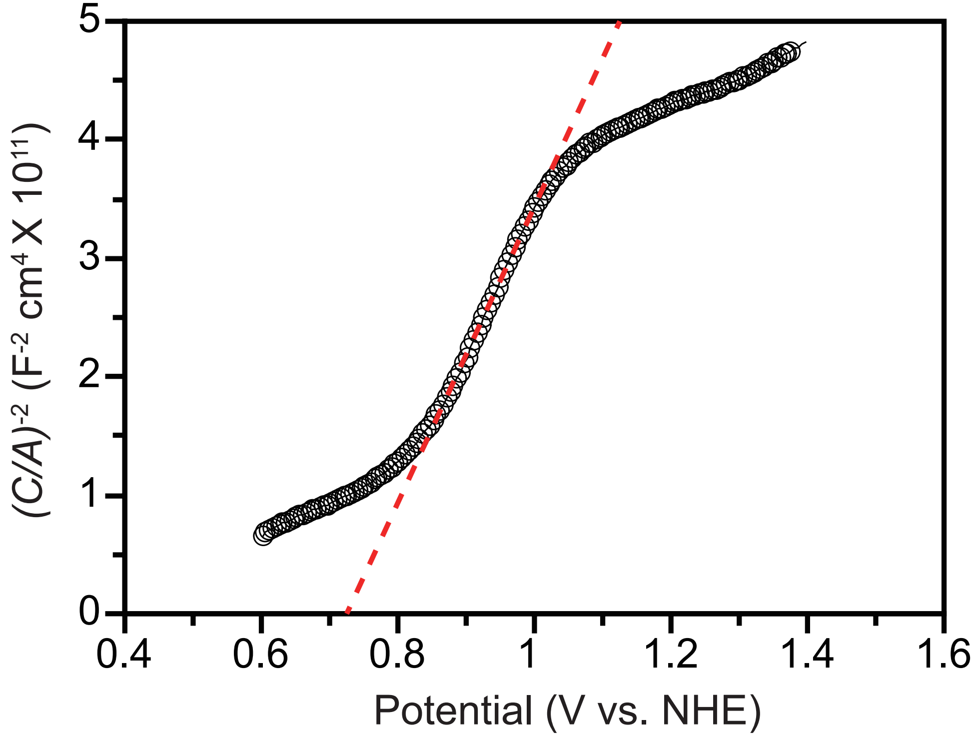


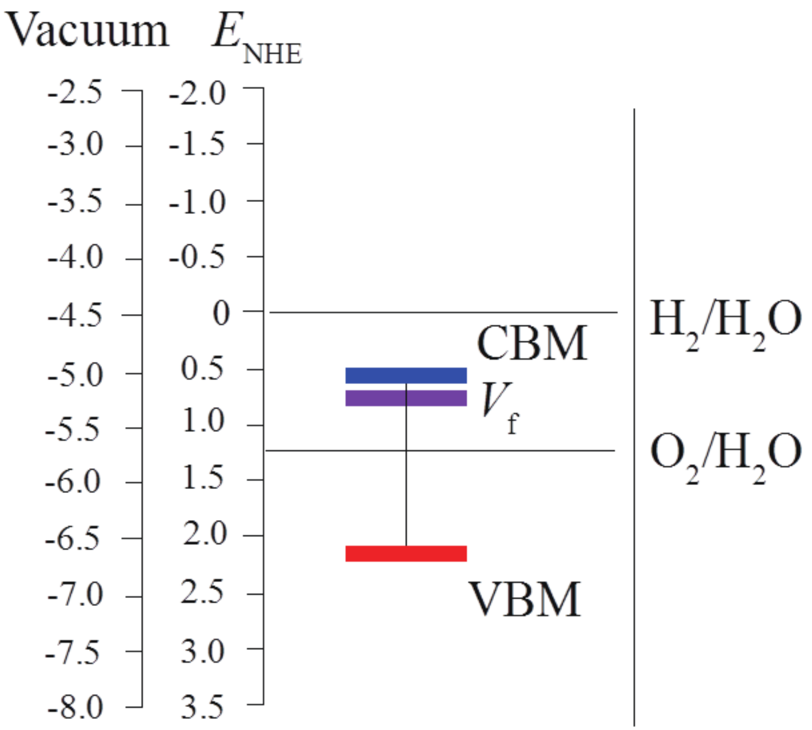


EDS analysis of metal atom distribution of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film. Ba, Bi, and Nb concentrations are analyzed at five unique positions throughout the sample, with the scan direction indicated schematically by the black arrow in the TEM image.

Accomplishments and Progress

The new approach was approved by experimental synthesis and characterization

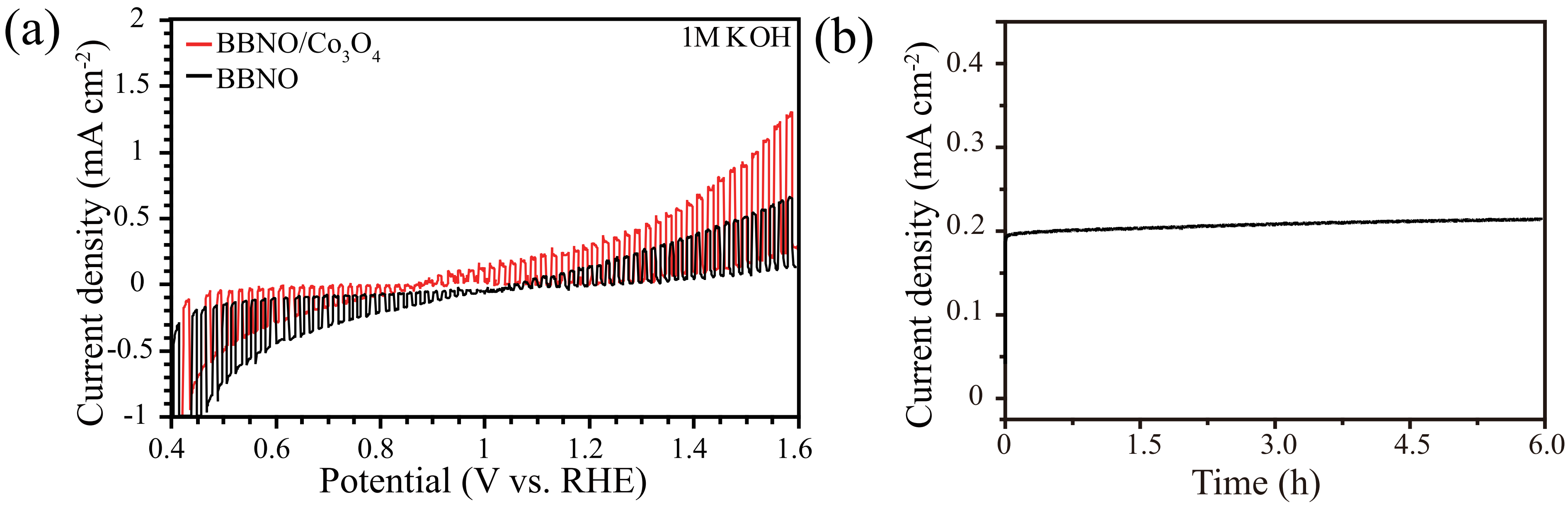




(Left) Mott-Schottky plots of measured $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film. (Right) Band position diagram of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ compared to the standard potentials of H_2 evolution and O_2 evolution according to the results of SE and Mott-Schottky plot. CBM: conduction band minimum, and VBM: valance band maximum.

Accomplishments and Progress

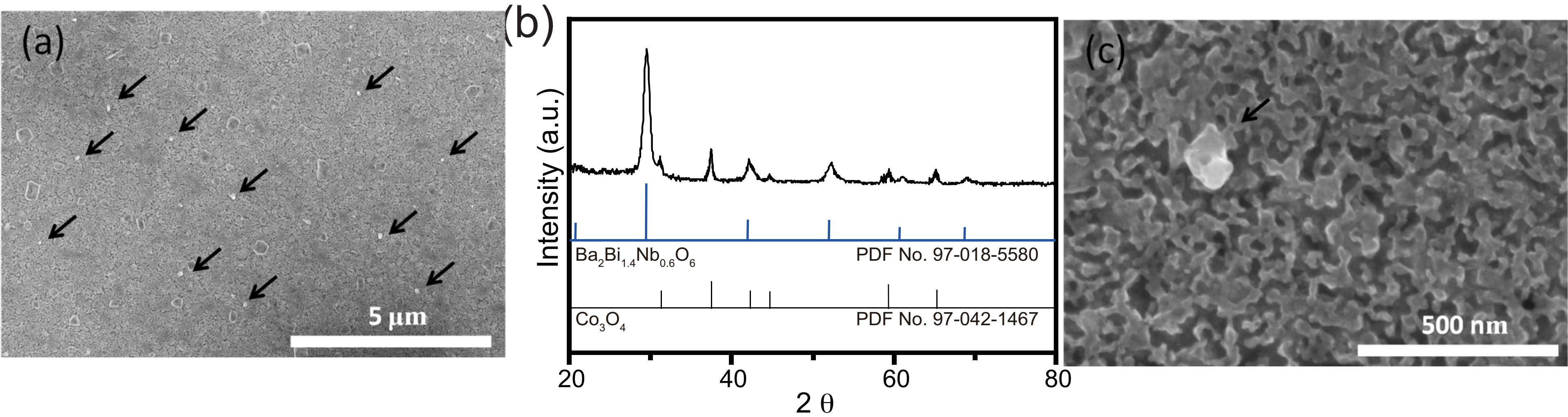
The new approach was approved by experimental synthesis and characterization



PEC water splitting performance of a $Ba_2Bi_{1.4}Nb_{0.6}O_6$ photoanode. (a) LSV curves of PEC water oxidation in 1 M KOH solution of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film and Co_3O_4 coated $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film (Pt, as counter electrode and cathode); (b) Durability test of the $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film at 1.23 V (vs RHE).

Accomplishments and Progress

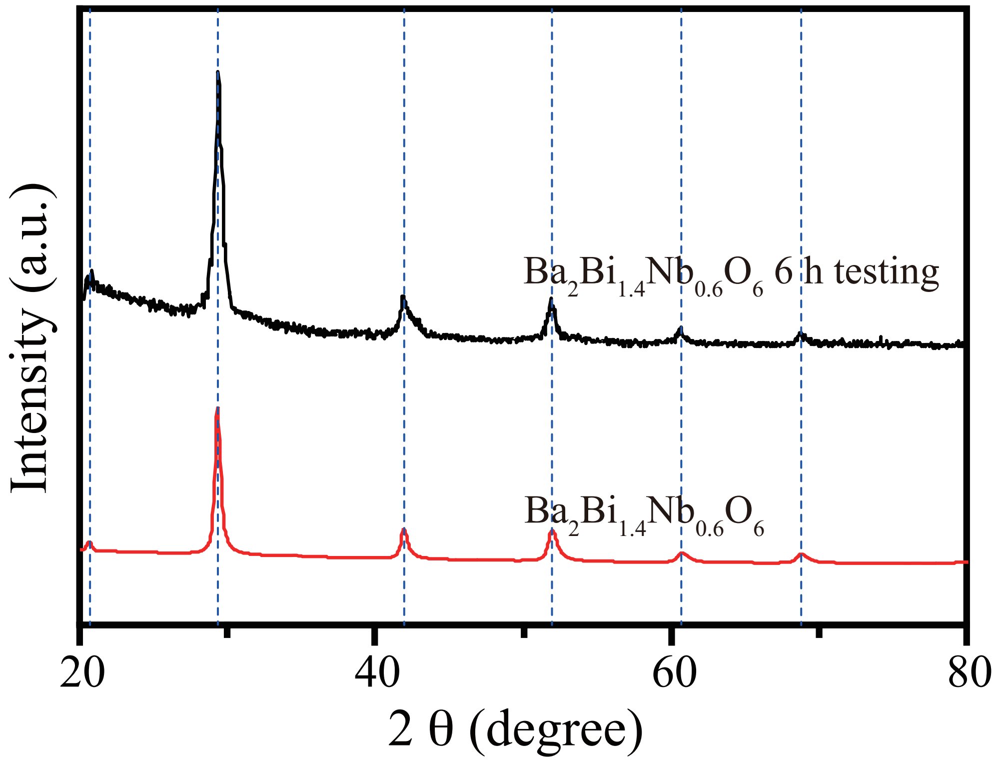
The new approach was approved by experimental synthesis and characterization



SEM image (a) and XRD pattern of Co_3O_4 nanoparticles coated $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film. Representative Co_3O_4 nanoparticles are marked with black arrows and the corresponding XRD pattern show both $Ba_2Bi_{1.4}Nb_{0.6}O_6$ and Co_3O_4 phases without any other impurities. Magnified view of single nanoparticle (c) shown with BBNO surface nanostructure also visible.

Accomplishments and Progress

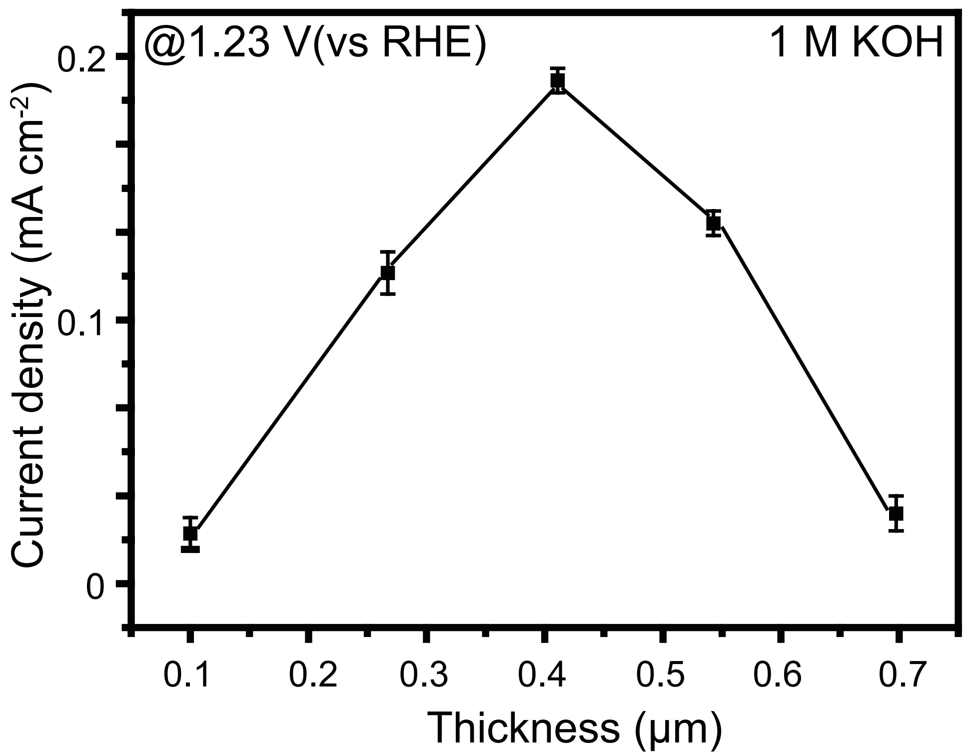
The new approach was approved by experimental synthesis and characterization



XRD patterns of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ sample before and after durability test.

Accomplishments and Progress

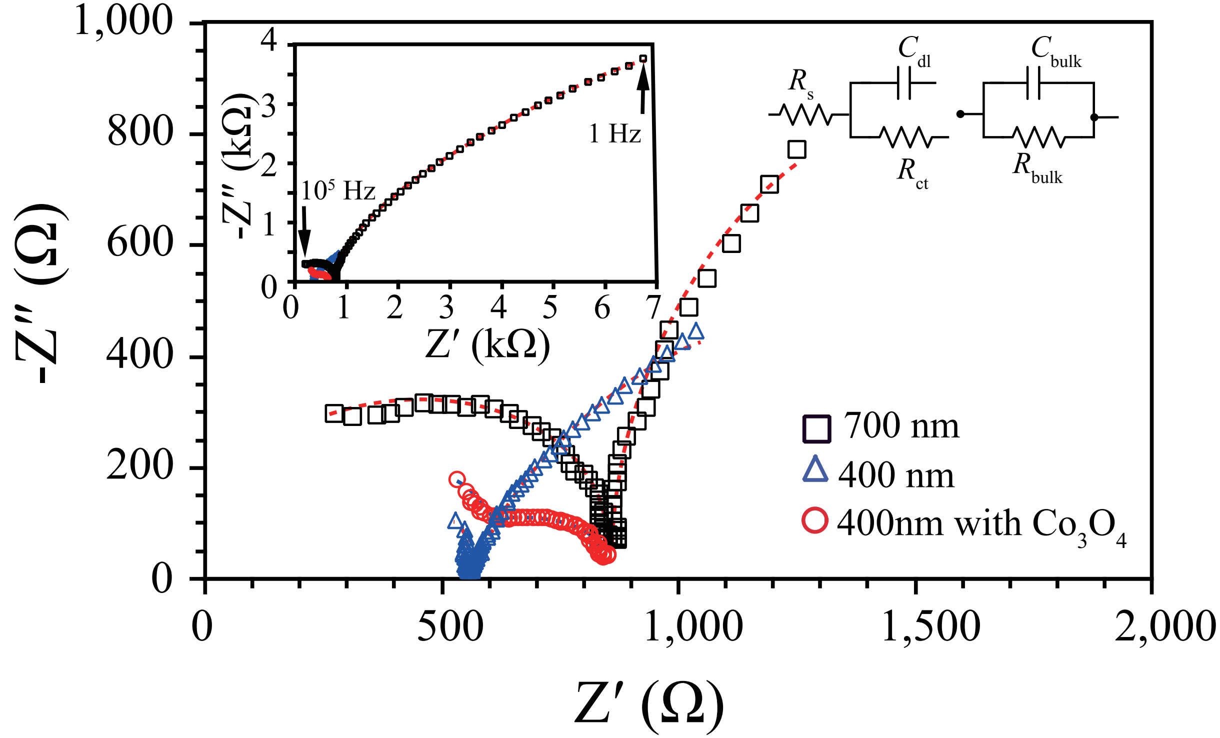
The new approach was approved by experimental synthesis and characterization



Dependence of photocurrent densities with the thickness of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film.

Accomplishments and Progress

The new approach was approved by experimental synthesis and characterization



Magnified Nyquist plot of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ film at various thickness (Black squares: 700 nm; blue triangles: 400 nm and red cycles: 400 nm with Co_3O_4 co-catalysts) at 1.3 V (vs RHE) in 1 M KOH under illumination. Inserted plot: full range Nyquist plot. Inserted Circuit model: R_s, R_{bulk}, R_{ct}: circuit resistance external to the specimen, electrode, and charge transfer resistance, respectively. C_{bulk} and C_{dl}: electrode capacitance and double-layer capacitance, respectively. Dash lines: Fitted EIS curves according to the circuit model inserted.

Accomplishments and Progress

The new approach was approved by experimental synthesis and characterization

Comparison of PEC performances of $Ba_2Bi_{1.4}Nb_{0.6}O_6$ and other reported planar metal oxide films

Samples	Photocurrent density ($mA\ cm^{-2}$) at 1.23 V vs. RHE	Onset potentials (V vs. RHE)	References
$Ba_2Bi_{1.4}Nb_{0.6}O_6$	0.2	1.05	*This work*
Fe_2O_3	0.11	0.4	*Nano Lett.* 2012, *12*, 6464
TiO_2	0.1	-0.4	*Nano Lett.* 2013, 13, 1481
$SrTiO_3$	0.04	-0.4	*J. Phys. Chem. C*, 2014, *118*, 25320
$BiVO_4$	~0.17	~0.8	*Phys.Chem.Chem.Phys.* 2016, 18, 5091
$BiVO_4$	~0.13	~0.9	*Int. J. Hydrogen Energ.* 2016, 41, 12842
$Bi2MoO_6$	~0.04	~0.9	*Phys.Chem.Chem.Phys.* 2016, 18, 5091

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

- A new approach has been proposed to engineer the bandgap of BBNO oxide double perovskites.

- An experimental bandgap of 1.64 eV was achieved by control the composition ($Ba_2Bi_{1.4}Nb_{0.6}O_6$) of BBNO thin films.

- Thin-film $Ba_2Bi_{1.4}Nb_{0.6}O_6$ photoanodes have demonstrated good PEC water splitting performances