Textured nanostructured Mo:$BiVO_4$ photoanodes with near unity carrier separation and high catalytic efficiency towards oxygen evolution

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Abstract

Improving the intrinsic electronic and catalytic properties of $BiVO_4$ has remained a challenge and tackling this will help us understand oxygen evolution photocatalysis in general . Here we report $BiVO_4$ photoanodes with a near unity carrier separation and record catalytic activity towards oxygen evolution. The high carrier separation results in photoanodes with high fill factors making them ideal for current matching in tandem water splitting devices. Crystallographic texturing of the {004} enables efficient hole extraction as well as shows a dramatically lower concentration of in-gap defect states. This study paves the way towards a new approach in designing highly efficient photoanodes for oxygen evolution.

Why $BiVO_4$?

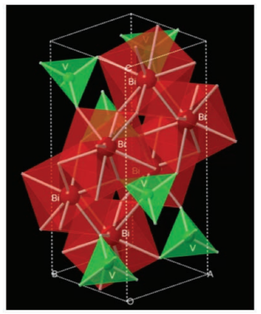
Pros :

- E_g ~ 2.4 eV , *n*-type
- α > 20,000 cm^{-1} for hv > 2.6eV
- E_C ~ 0 V and V_{fb} < 0.2 V vs RHE [1]
- L_p ~ 100nm [2]
- earth abundant , nontoxic , cheap

Cons :

- $L_D < \alpha^{-1}$ (inadequate transport)
- poor water oxidation kinetics [3]
- limited stability
- non-optimal E_g (1.8-2.0 eV best)

Common yellow pigment



I2/b (Scheelite, monoclinic)
5.196 x 5.094 x 11.705 Å

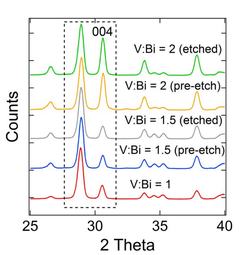
Fabrication of Mo/T $BiVO_4$ photoanodes

dissolve 0.6 mmol $Bi(NO_3)_3$ in EG, [add 0.012 mmol $MoO_2(acac)_2$]
↓ sonicate 5 min
add acetic acid & water
↓ sonicate 10 min
add 0.12 mmol $VO(acac)_2$
↓ sonicate 10 min
add Pluronic F108 block copolymer
↓ sonicate 30 min
spincoat and anneal (475°C , 15min)

KOH etch of V_xO_y →

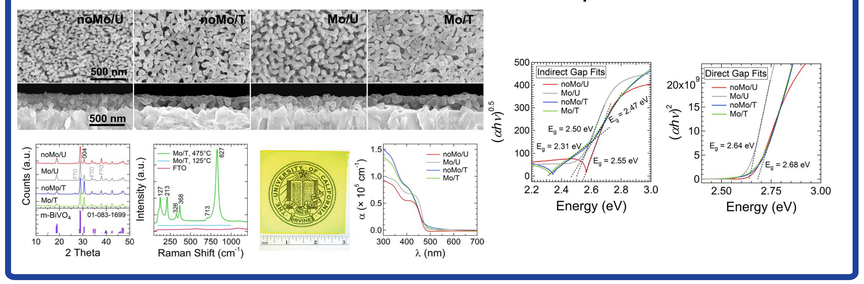
$BiVO_4$ / quartz thin film

- Single step deposition
- Simple and reproducible over large areas
- High surface area films (nanostructured)
- Robust and optically flat films
- Tunable thickness
- Tunable composition

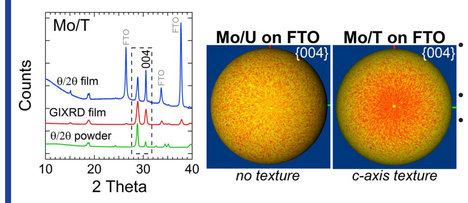


- Texturing in the films can be controlled by changing the Bi:V precursor ratio in the ink.
- The degree of texturing is thickness dependent.
- The presence of Mo has no effect on the texturing.

Different flavors of $BiVO_4$

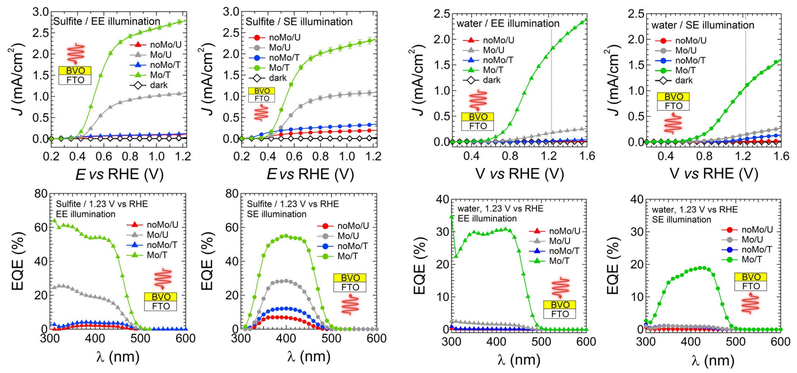


Proof of texturing : In-plane pole figure



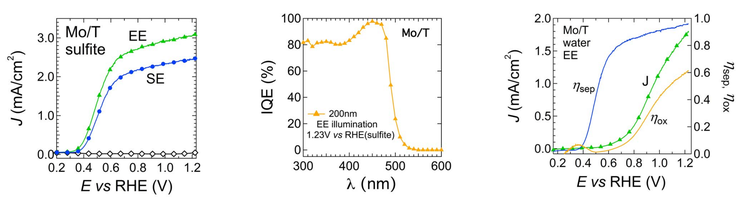
- Absence of enhancement in {004} intensity in the BB powder confirms texturing effect.
- Texturing is independent of Mo addition.
- The directionality of texturing is substrate dependent , FTO shows an out-of plane texture while quartz substrate show an in-plane texture.

Sulfite *vs* water oxidation



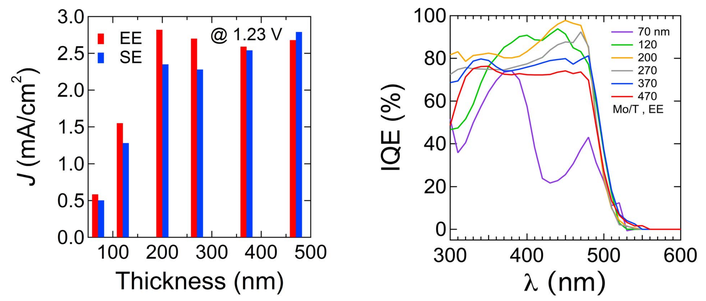
- Sulfite being a hole scavenger shows higher photoresponse than water oxidation.
- Front-illuminated devices(EE) perform better for both sulfite and water oxidation.

Unity charge extraction and record catalytic activity

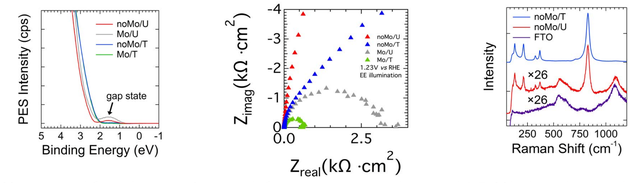


- Separation efficiency is high as 80% at low bias conditions (0.6V vs RHE) and nearly 100% at OER.
- IQE for 200 nm Mo/T films rises sharply at band edge and is on an average of 90% above the band edge.

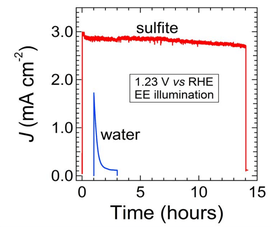
Thickness dependence of photoresponse



Mechanism for enhanced performance and stability



- Untextured films have an in-gap defect state centered around 0.7eV below the conduction band edge.
- In-gap defect states are absent in textured films and have been assigned to oxygen vacancies via hydrogen dosing experiments.
- Impedance spectroscopy was used to confirm low charge transfer resistance.
- The 25x increase in Raman signal for the textured electrodes is attributed to lack of phononic scattering from the in-gap defect states.



- High stability towards sulfite oxidation.
- Water oxidation stability is substantially lower but still best among all $BiVO_4$-uncatalyzed photoanodes.

Conclusions and Future Work

- Simultaneous texturing and Mo addition results in superior carrier separation in $BiVO_4$
- Onset potential for water oxidation is ~ 0.53 V vs RHE which is one of the lowest reported for standalone uncatalysed $BiVO_4$ emphasizing the sizeable enhancement in the catalytic properties of the photoanode.
- Lower density of in-gap defect states coupled with a lower activation energy for H_2O adsorption on the {004} facet[4] is the reason for the observed enhancement.
- Future work will be focussed on improving the onset potential for water oxidation in the absence of a catalyst as well as improve the stability towards water oxidation.

References

[1] Park Y., McDonald K.J., Choi K.S., Chem.Soc.Rev., 2013, 42, 2321-2337.
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