ELECTROCHEMICAL DEPOSITION OF $BiVO_4$ ON QUARTZ-BASED TRANSPARENT, CONDUCTIVE, POROUS SUBSTRATES FOR SOLAR GAS-PHASE WATER SPLITTING APPLICATIONS

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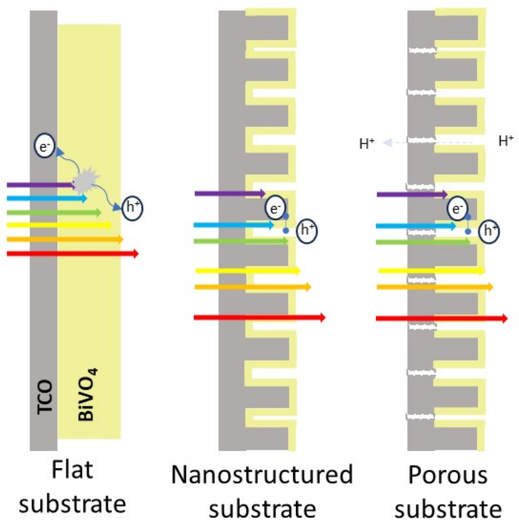
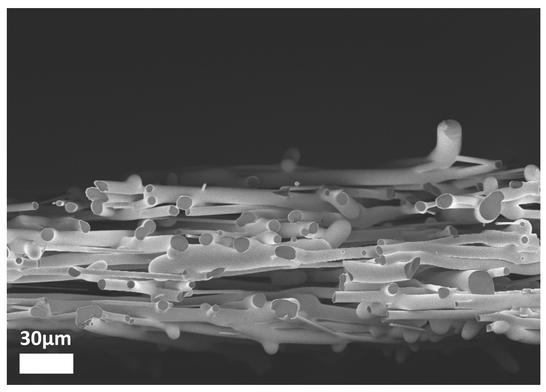
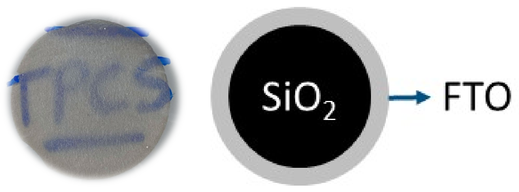
Abstract

Bismuth vanadate is one of the most promising photoanode materials for overall water splitting and is known for its high visible light photoactivity and good stability [1]. However, it suffers from recombination due to the modest diffusion length of the photogenerated charge carriers. To avoid this problem, nanostructuring the substrate will improve the light absorption length while shortening the charge diffusion length [2]. Further improvements can be made by using a porous substrate, which enables efficient transport of protons/hydroxide ions from one electrode to the other. Our project partners from the EU H2020 project "Sun-to-X" developed a transparent, porous conducting substrate (TPCS) made of quartz fiber coated with a FTO layer [3]. An electrochemical deposition technique was used for conformal coating of $BiVO_4$ on TPCS. This work explains the challenge of diffusion limitation within the porous substrate and the importance of the nucleation step.

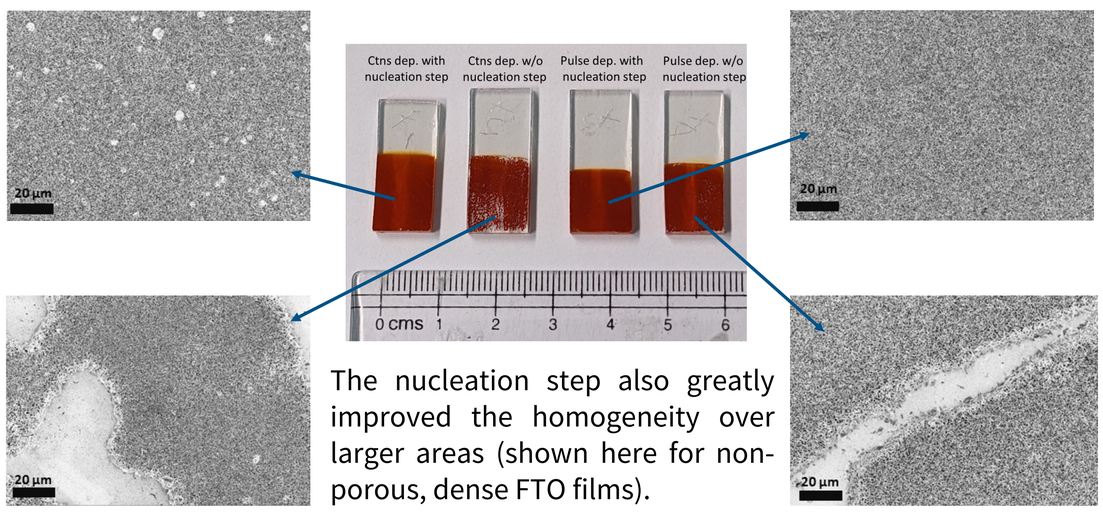
Motivation





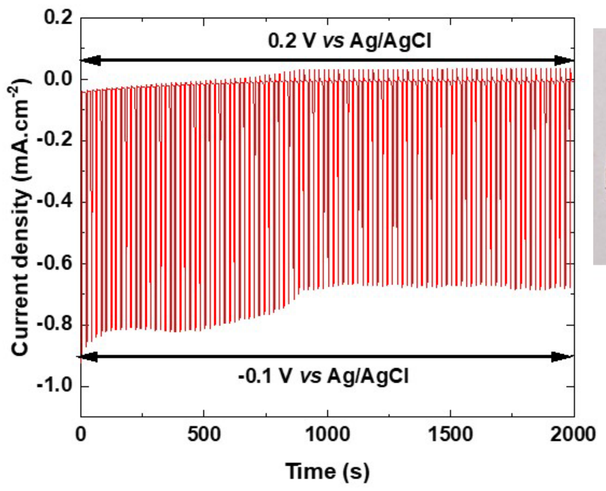


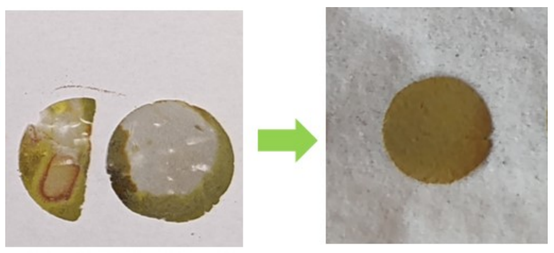
Why nucleation step is important?



The nucleation step also greatly improved the homogeneity over larger areas (shown here for non-porous, dense FTO films).

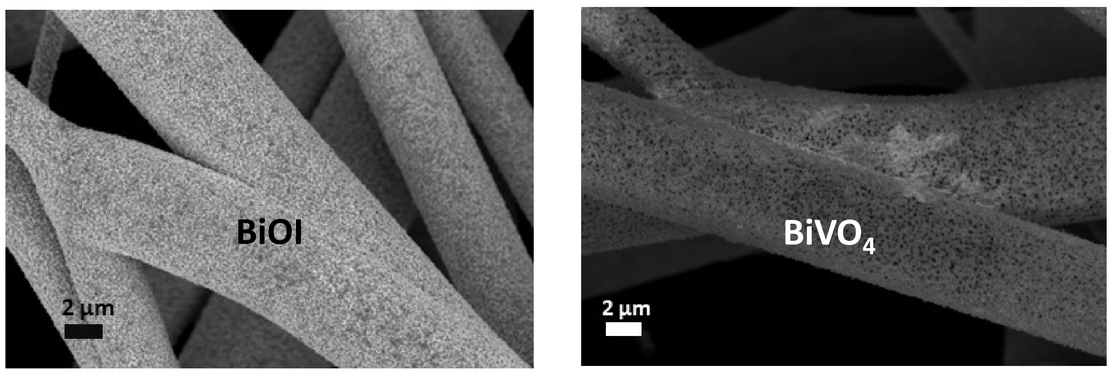
Continuous vs Pulsed electrodeposition





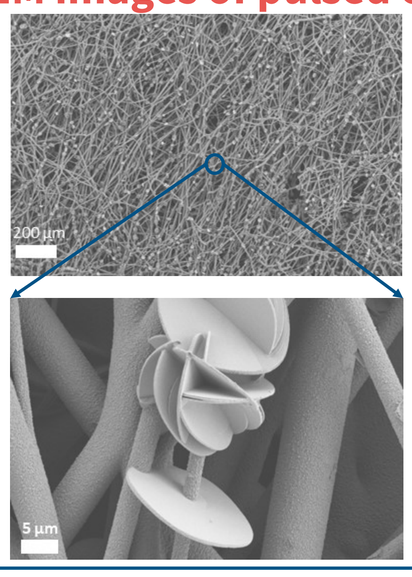
Adopted from Choi's group [4], $BiVO_4$ was made by BiOI electrodeposition followed by V addition. By using pulsed electrodeposition, we could mitigate mass transfer limitations within TPCS.

Pulsed deposition with nucleation step



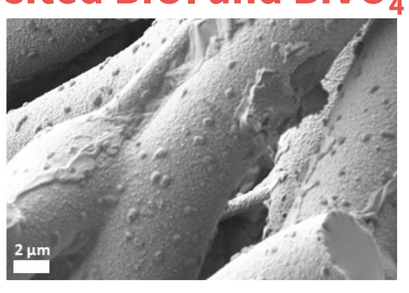
Pulsed electrochemical deposition of BiOI on TPCS combined with a nucleation step results in homogeneous and uniform coverage of the TPCS surface with both BiOI and the resulting $BiVO_4$ film.

SEM images of pulsed electrodeposited BiOI and $BiVO_4$



Addition of V precursor

Annealing at 500 °C



Without a separate nucleation step at -0.35 V vs. Ag/AgCl, BiOI did not nucleate homogeneously over the TPCS surface. Instead, isolated $BiVO_4$ islands and the undesired V_2O_5 phase were found after adding the $VO(acac)_2$ vanadium precursor, annealing at 500 °C.

Conclusion

- We successfully used pulsed electrochemical deposition of BiOI to improve the slow mass transfer of active species from the bulk of the electrolyte to the surface of TPCS.
- The nucleation step at -0.35 V vs. Ag/AgCl was found to be essential for obtaining homogeneous films over larger areas.
- By combining pulsed electrodeposition with the nucleation step, the BiOI precursor layer could be homogeneously deposited onto the TPCS support. Post-deposition treatment of this layer with the vanadium precursor resulted in the desired uniform $BiVO_4$ films.

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ACKNOWLEDGEMENT AND PARTNERS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 883264

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