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# Cerium titanates: An unexplored class of UV-visible light active photoanodes for water splitting

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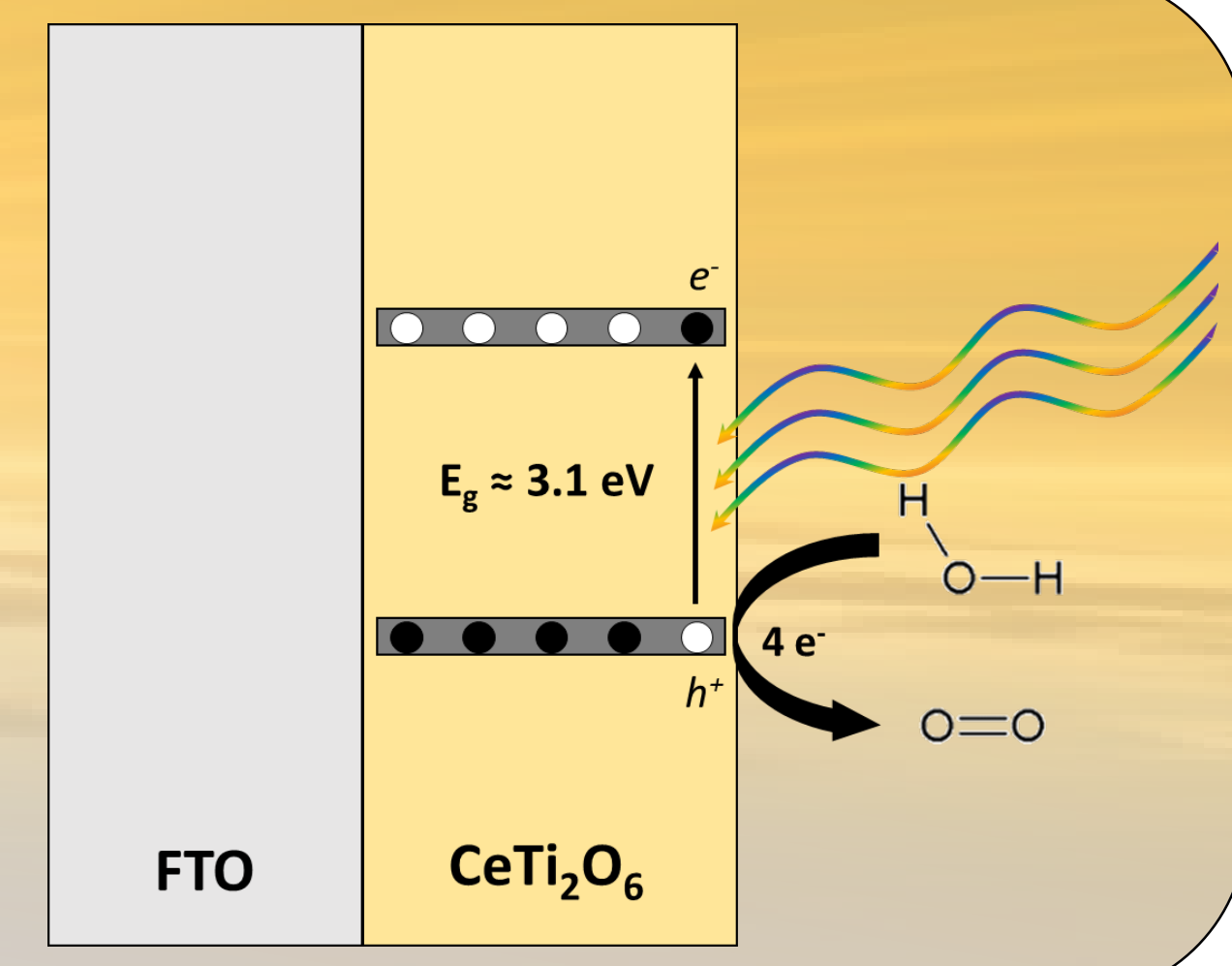
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## Introduction

Photoelectrochemical water splitting is hoped to become a competitive source of green hydrogen, but there is still a need to discover novel photoelectrode materials [1].

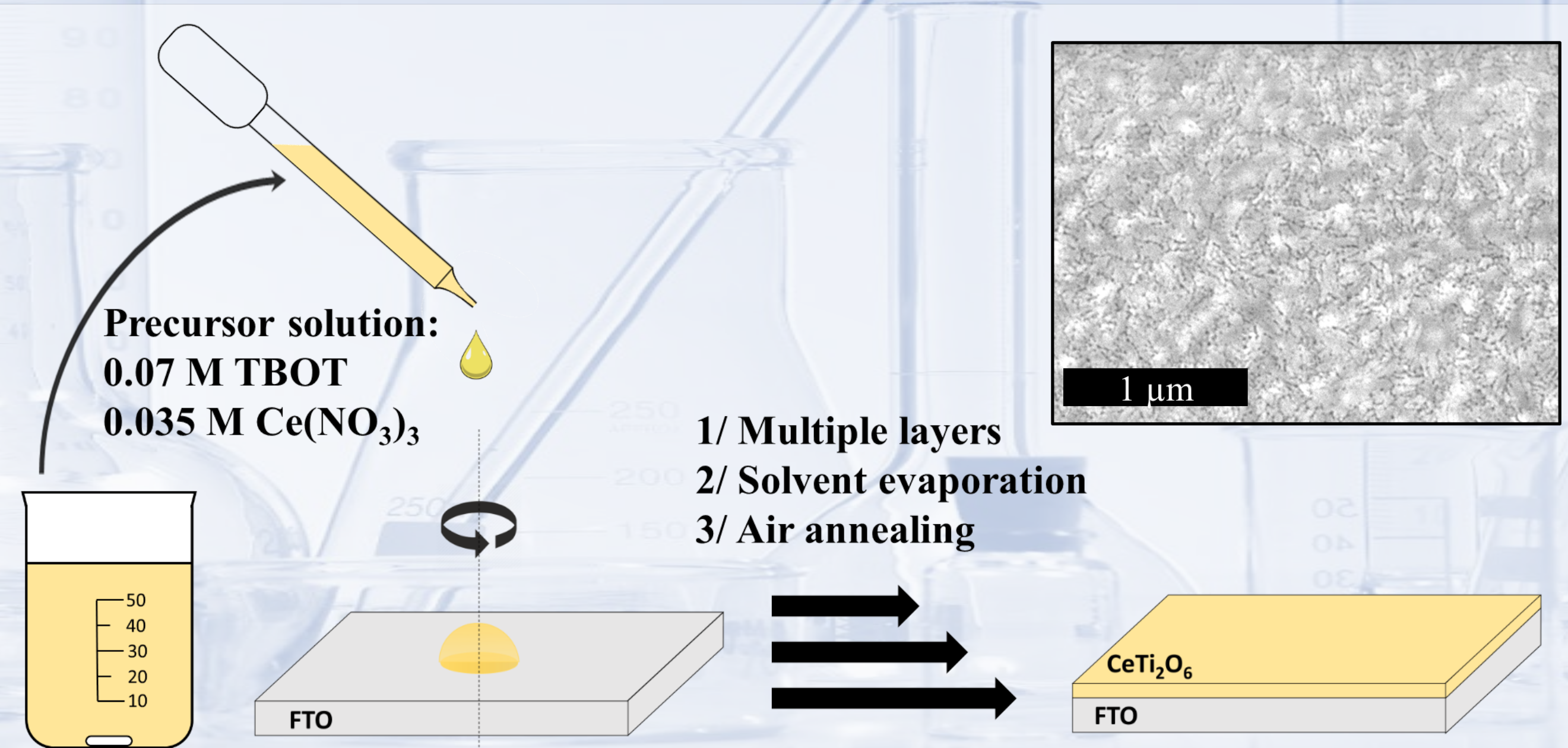
Cerium titanates, especially  $\text{CeTi}_2\text{O}_6$  brannerite, have drawn interest due to their photocatalytic activity [2] and thermochemical hydrogen production potential [3].

We propose to describe the photoelectronic properties of  $\text{CeTi}_2\text{O}_6$  for a potential use in photoelectrochemical water splitting.

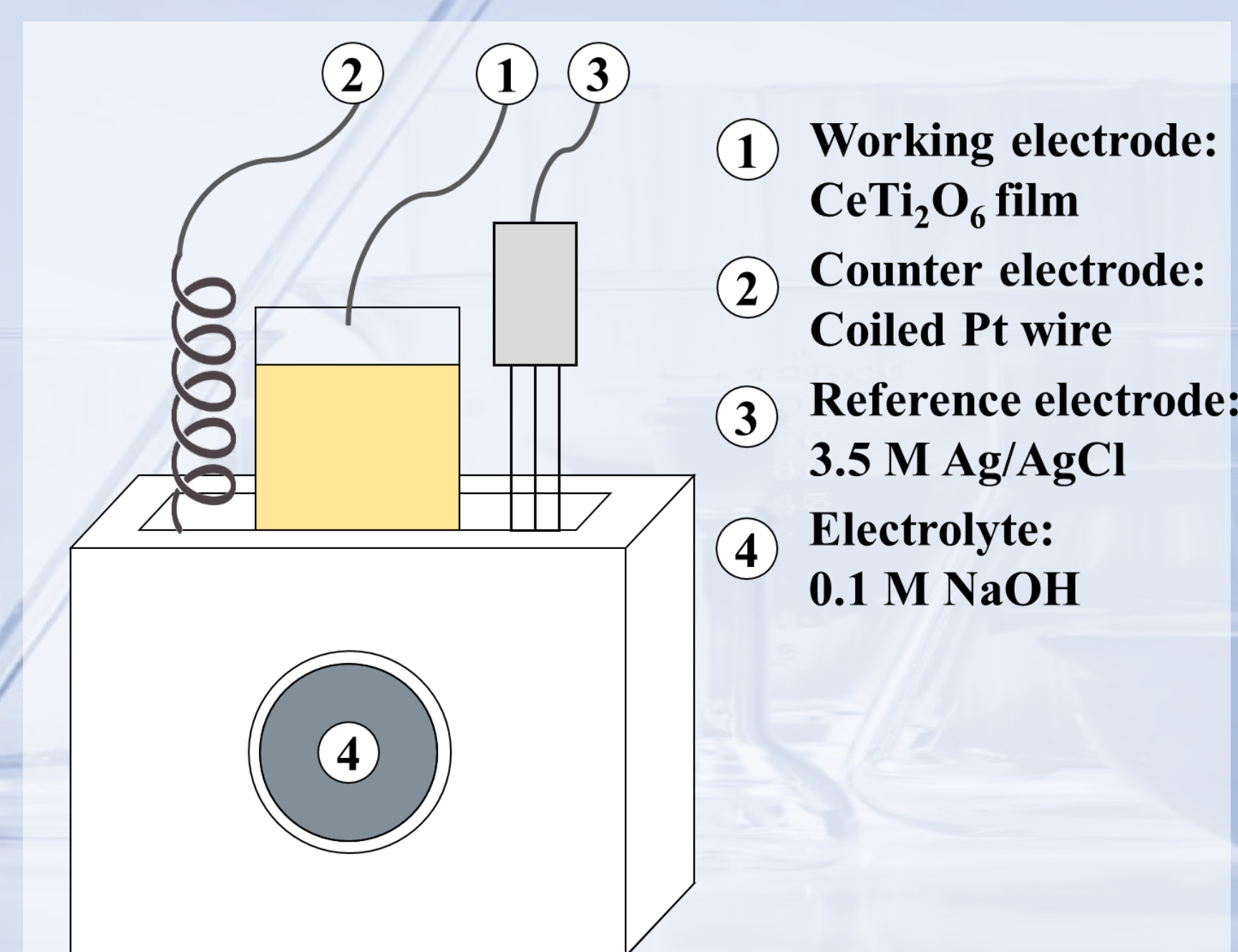


## Materials and methods

- Thin films were prepared by spin-coating of a precursor solution and subsequent annealing at  $700^\circ\text{C}$



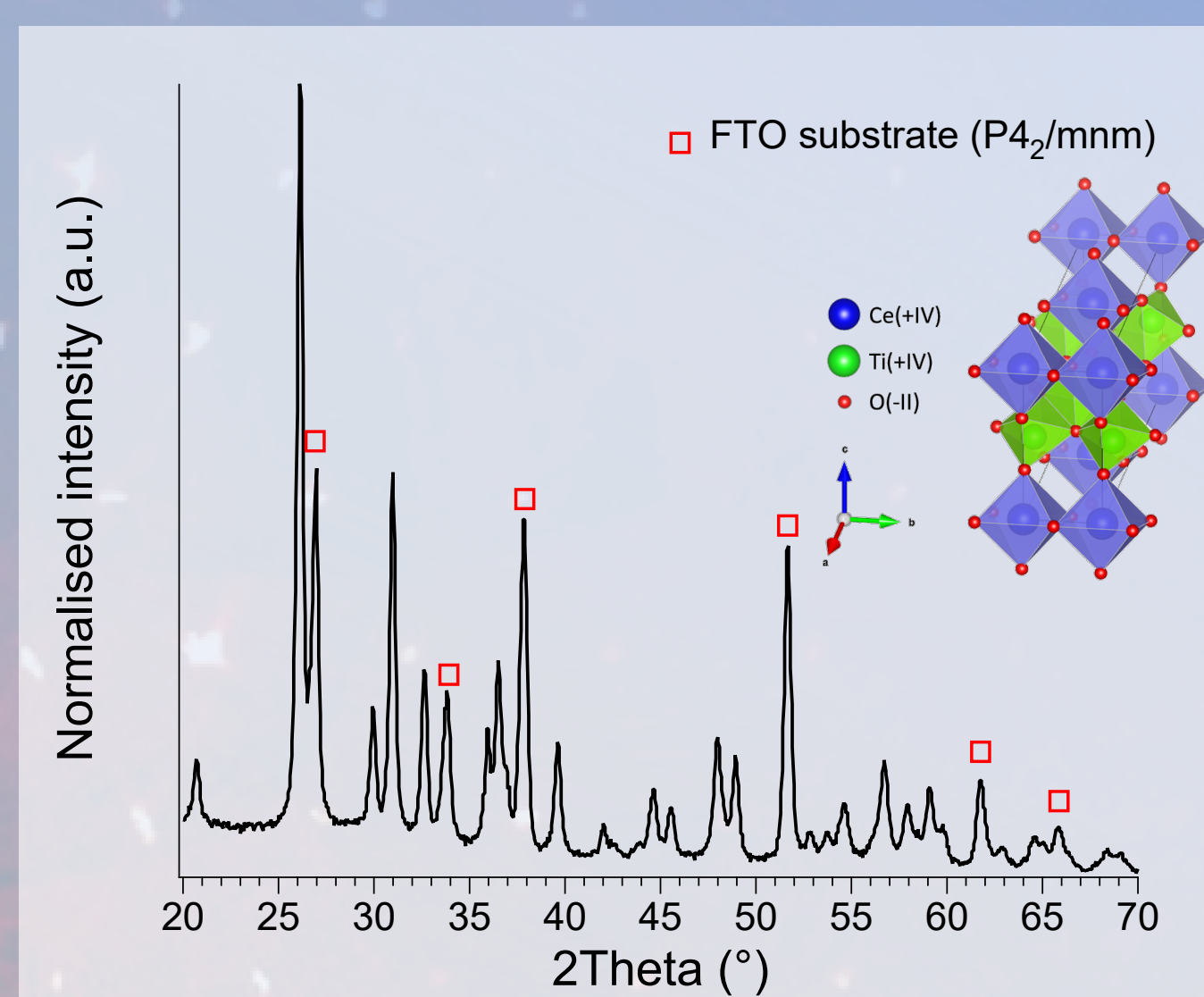
- Photoelectrochemical measurements were performed with a homemade cell under a Xe arc lamp illumination (approx. 1 sun irradiance)



Chopped light linear sweep voltammetry (LSV)  
Scan rate:  $20 \text{ mV} \cdot \text{s}^{-1}$   
2s ON/OFF

## Brannerite structure

- GIXRD confirmed the successful synthesis of pure  $\text{CeTi}_2\text{O}_6$  brannerite thin films at a lower temperature than usually reported
- The Brannerite family crystallises in a monoclinic Bravais lattice and belongs to the space group  $C/2m$



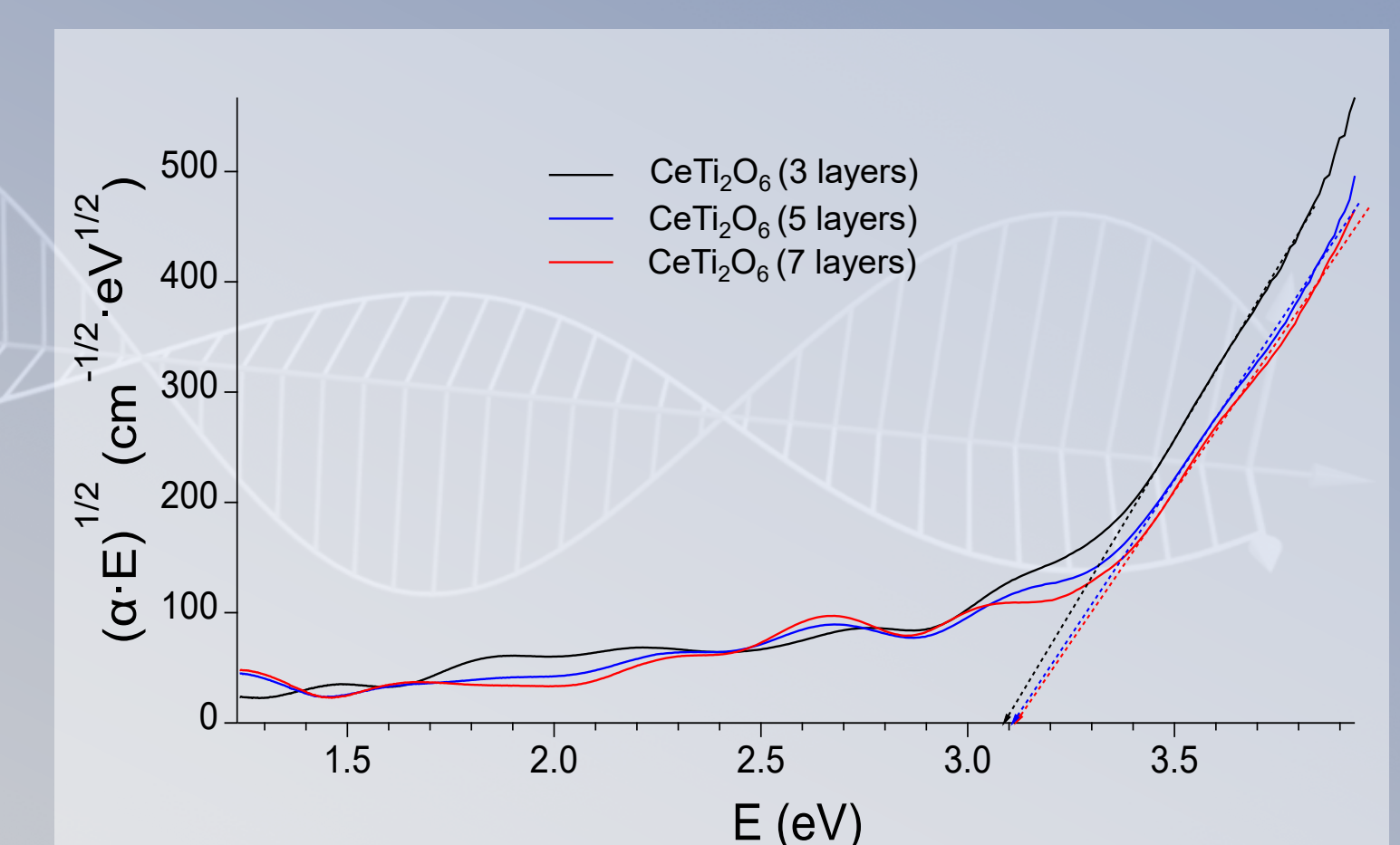
## Optical band gap

- Transmittance UV-Vis was used to determine the band gap ( $E_g$ ):

$$\alpha_{\text{Film}} = \frac{1}{d_{\text{Film}}} \cdot \left( \ln \left( \frac{1}{T} \right) - \alpha_{\text{FTO}} \cdot d_{\text{FTO}} \right)$$

$$\alpha_{\text{Film}} \cdot E = A \cdot (E - E_g)^2$$

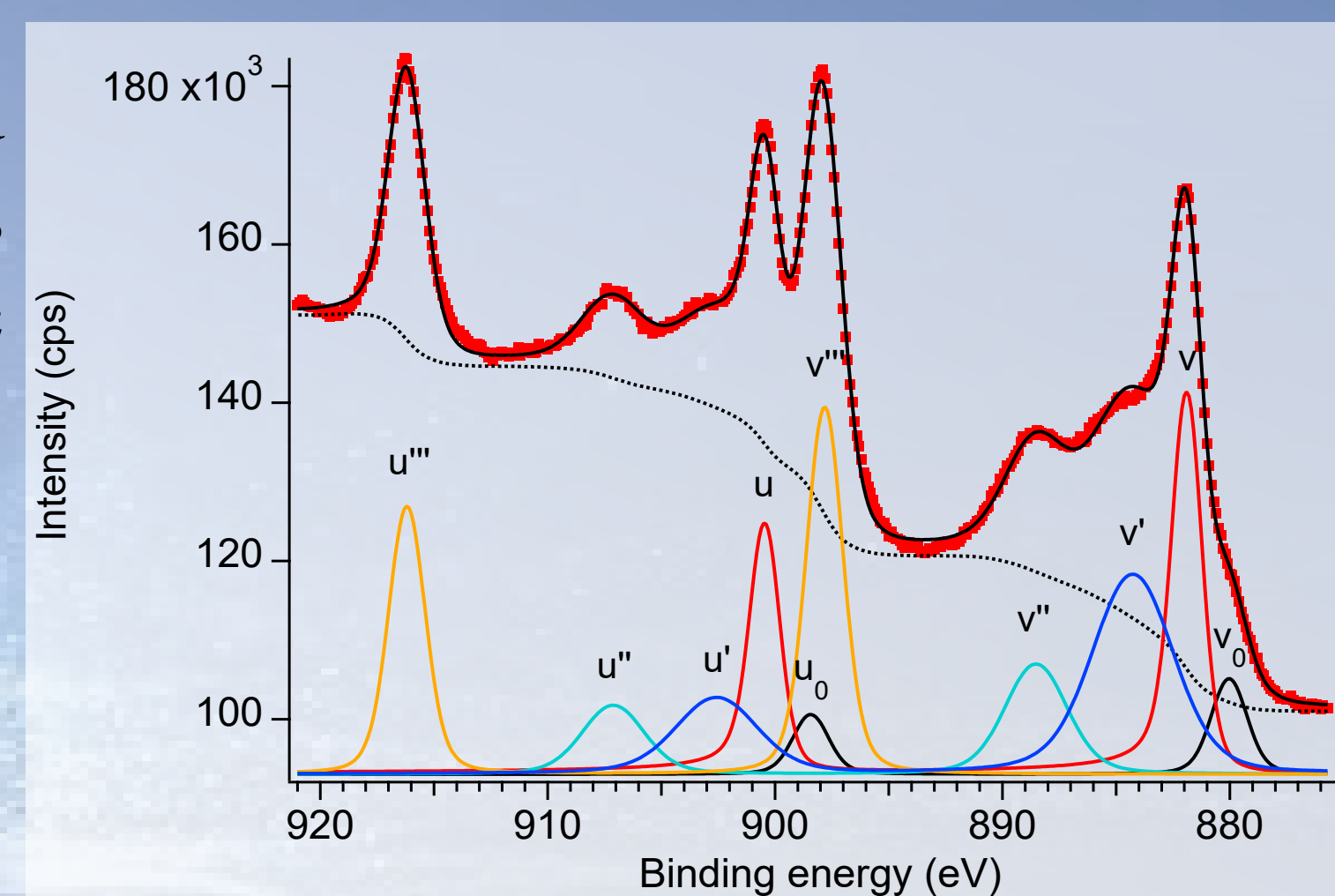
- An indirect band gap of about 3.1 eV was found with the Tauc plot



## Surface cerium states

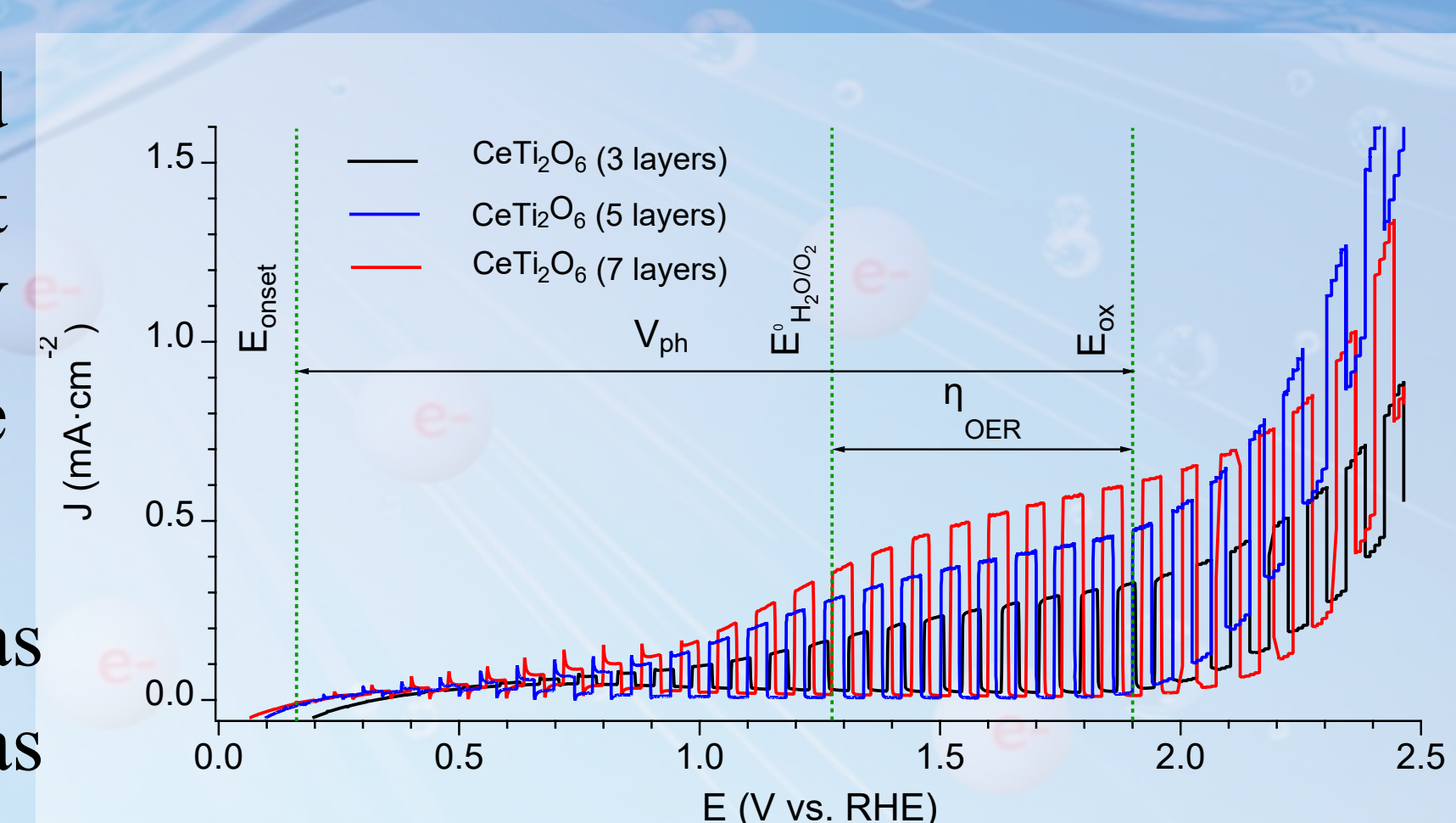
- XPS of the Ce3d region showed that 40% of surface cerium ions were in the non-stoichiometric valency +III

Peak assignment	Binding energy (eV)	Ce species	Relative area (%)
$u''''$	880	$\text{Ce}^{3+}$	7.1
$v_0$	881.9	$\text{Ce}^{3+}$	9.6
$v'$	884.3	$\text{Ce}^{3+}$	13.4
$v''$	888.6	$\text{Ce}^{3+}$	11.9
$v''''$	897.8	$\text{Ce}^{3+}$	10.6
$u_0$	898.4	$\text{Ce}^{3+}$	7.5
$u_1$	900.5	$\text{Ce}^{3+}$	8.8
$u'$	902.6	$\text{Ce}^{3+}$	11.5
$u''$	907	$\text{Ce}^{3+}$	11.5
$u''''$	916.2	$\text{Ce}^{3+}$	8.1



## Photoelectrochemical behaviour

- $\text{CeTi}_2\text{O}_6$  thin films produced a promising photo-current ( $0.3 \text{ mA} \cdot \text{cm}^{-2}$  at  $E = 1.23 \text{ V}$  vs. NHE) and photovoltage (1.74 V)
- Photocurrents increased as the film thickness was increased



## Conclusions and prospects

- A new type of photoelectrode suitable for the oxygen evolution reaction has been proposed and showed promising photoelectrochemical properties
- The band structure and alignment is yet to be determined for further optimisation of the materials' performances
- Upon these results, the addition of surface electrocatalysts and matrix alloyants will be considered

[1] *Nat. Rev. Mater.* 2016, **1**, 15010

[2] *JSST.* 2018, **8**, 202-2010

[3] *ACS Appl. Mater. Interfaces* 2020, **12**, 19, 21521–21527