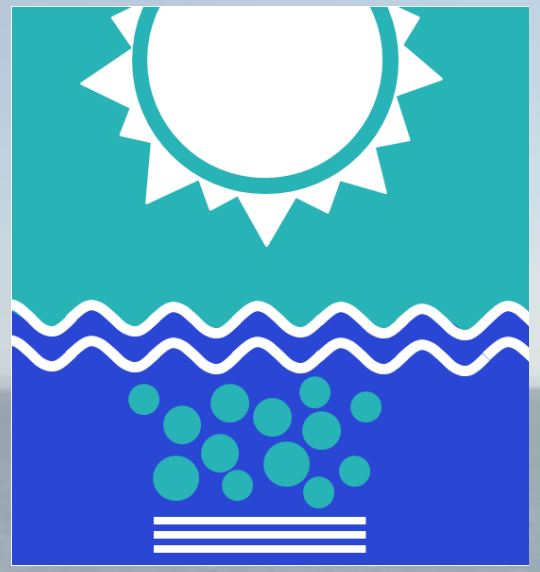
UNIVERSITY OF WARSAW

UW Two centuries Good beginning

CeNT CENTRE OF NEW TECHNOLOGIES

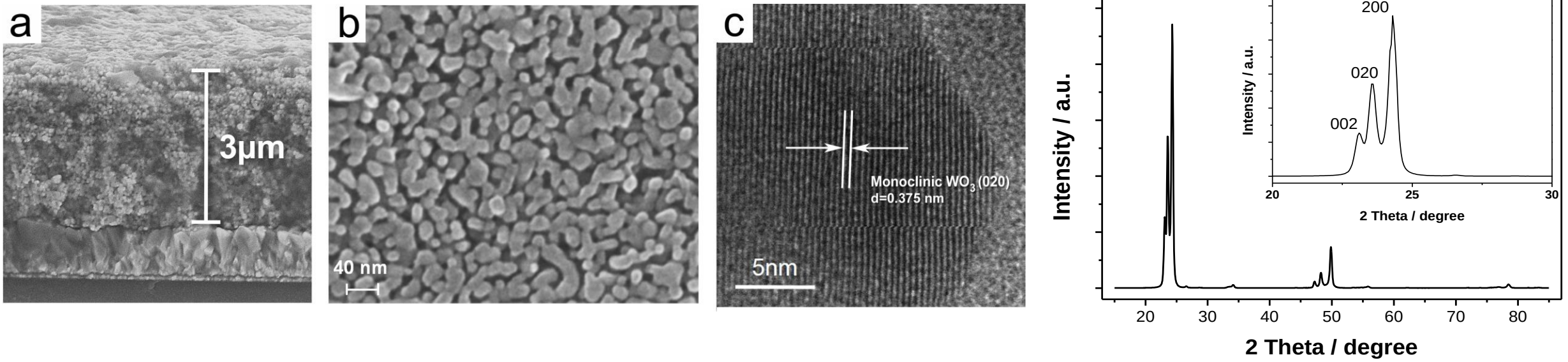
Laboratory of Photoelectrochemistry and Solar Energy Conversion

Jan Augustyński



Our activity focuses on investigation of photo-oxidation reactions occurring, under visible light, at n-type semiconductor electrodes that act as photoanodes in photoelectrochemical devices where, at the same time, hydrogen is formed at a metal cathode. Although the main effort is oriented towards water splitting, we investigate, in parallel, other reactions such as chlorine formation or oxidation of toxic/waste organic products.

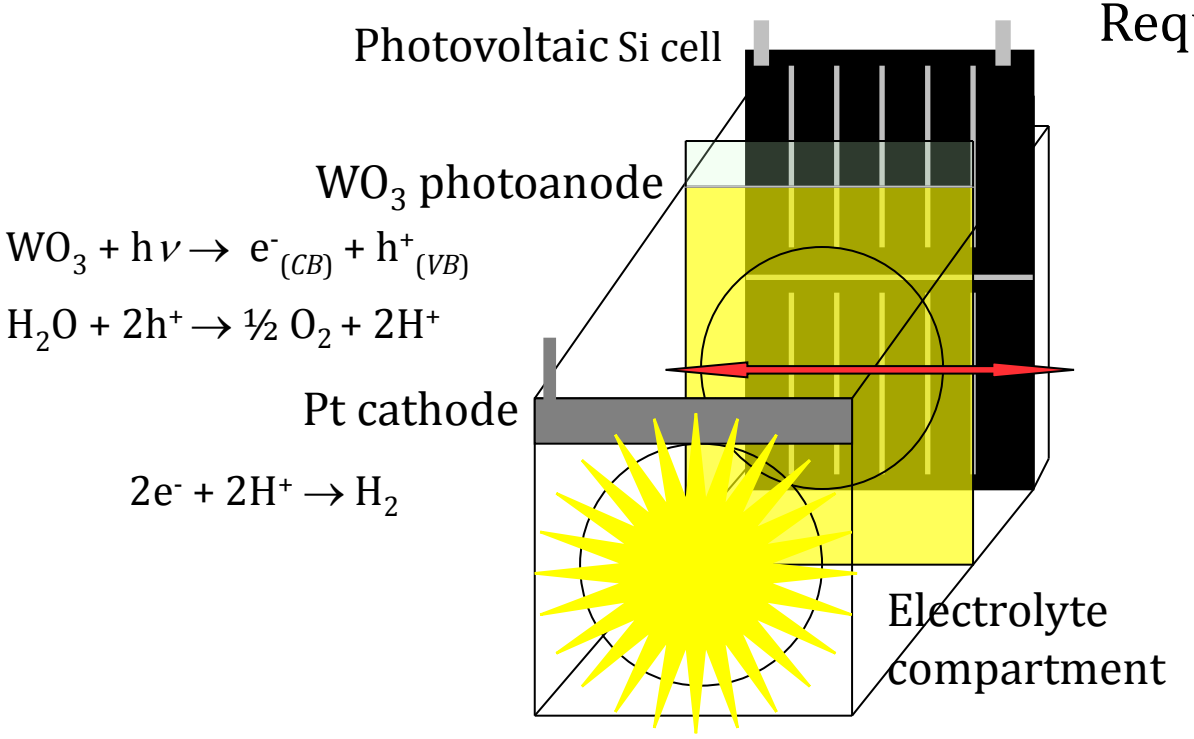
To optimize opto-electronic properties, we synthesize nanocrystalline (NC), porous semiconductor film electrodes. A regular porosity allows permeation of the whole electrode by the electrolyte. Excellent crystallinity is crucial to avoid charge carrier recombination among nanoparticles that form the film. The structure of a such electrode is shown below.



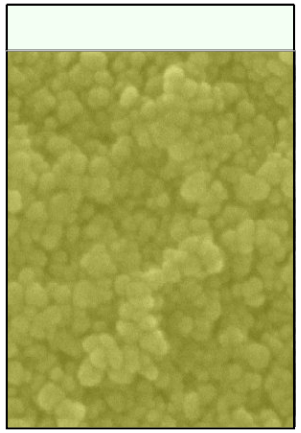
SEM and TEM images and XRD patterns of a typical NC tungsten oxide (WO_3) film formed by aqueous sol-gel method on F-SnO_2/glass (FTO) substrate.

Adv. Energy Mater. **2019**, *10*, 1903213.

Since none of the oxide semiconductor photoanodes, investigated till now, are able to directly split water in the presence of a metal cathode under visible light, we had developed the concept of a tandem device. Such a device involves two optical systems in series: the photoelectrolysis cell and a photovoltaic (PV) cell, placed behind, intended to provide the bias voltage required to split water in the first cell. As shown schematically below, the PV cell captures the complementary parts of the solar spectrum transmitted through the photo-electrolysis cell.



Requirements for an WO_3 photoanode:



- ✓ Semi-transparent
- ✓ Stable
- ✓ Homogeneous
- ✓ Thick enough

for efficient light absorption

J. Mater. Chem., **2008**, *18*, 2298.

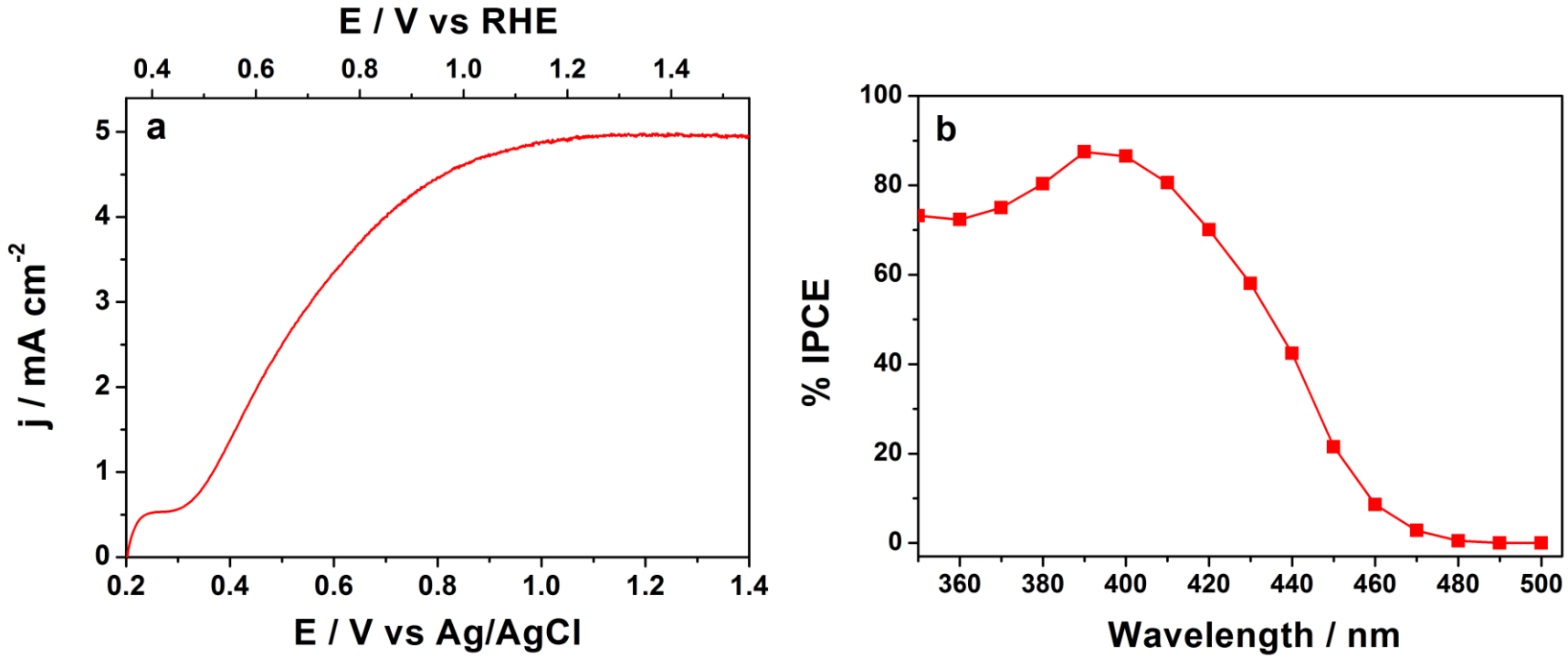
The concept of the tandem cell became viable due to the development in our laboratory of semi-transparent, nanoporous WO_3 film photoanodes that reach saturation photocurrents under an external bias (between the photoanode and metal cathode) of the order of 1 V.

Such a bias voltage can be provided by a number of single junction PV cells.

We validated in practice the operation of a tandem cell combining the WO_3 - Pt water splitting photocell with a dye-sensitized PV cell. *Nature Photon.* **2012**, *6*, 824.

The chemical (H_2) -to-solar efficiency demonstrated at that time was above 3%.

Recent advances we made in the design of formed NC WO_3 photoanodes, in particular, the modulated porosity of the film, allowed a large improvement of the water oxidation photocurrents that reached, as shown below, almost 5 mA cm^{-2} (4.8-4.9) in the saturation region.



a) Water oxidation current-potential plot (recorded under simulated AM 1.5G solar light) and b) the incident photon-to current efficiency spectrum for a 3 μm thick WO_3 photoanode both measured in a 1 M CH_3SO_3H electrolyte.

This result translates into a record high hydrogen-to-solar efficiency close to 6%.

Adv. Energy Mater. **2019**, *10*, 1903213.

The last generation of developed WO_3 photoanodes was employed in a recent study of photoelectrolysis of seawater. :

Highly efficient sunlight-driven seawater splitting in a photo-electrochemical cell with chlorine evolved at nanostructured WO_3 photo-anode and hydrogen stored as hydride within metallic cathode.

M. Jadwiszczak, K. Jakubow-Piotrowska, P. Kedzierzawski, K. Bienkowski, J. Augustynski

Adv. Energy Mater. **2019**, *10,* 1903213.

Context

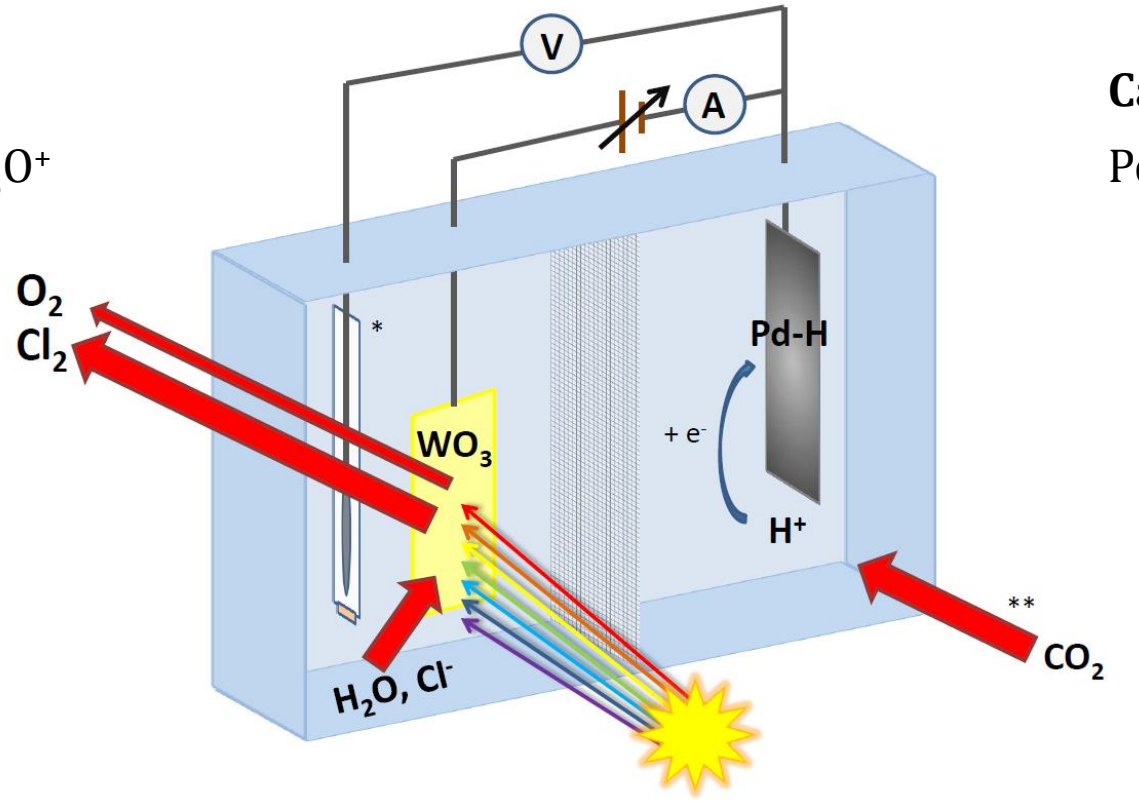
(Photo)electrolysis of water is broadly considered as a main (carbon-free) way to generate hydrogen. However, if electrolysis of fresh water is to be used - in the near future - to store a substantial portion of the world's energy, this would put heavy pressure on vital water resources. Since the seawater is a free and widely abundant electrolyte (*ca* 0.5 M NaCl), there were various attempts to use it both in photo-electrochemical (PEC) and conventional electrochemical devices to produce hydrogen.

Schematic diagram of the seawater splitting PEC

Anodic compartment

$H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H_3O^+$

$2Cl^- + 2h^+ \rightarrow Cl_2$



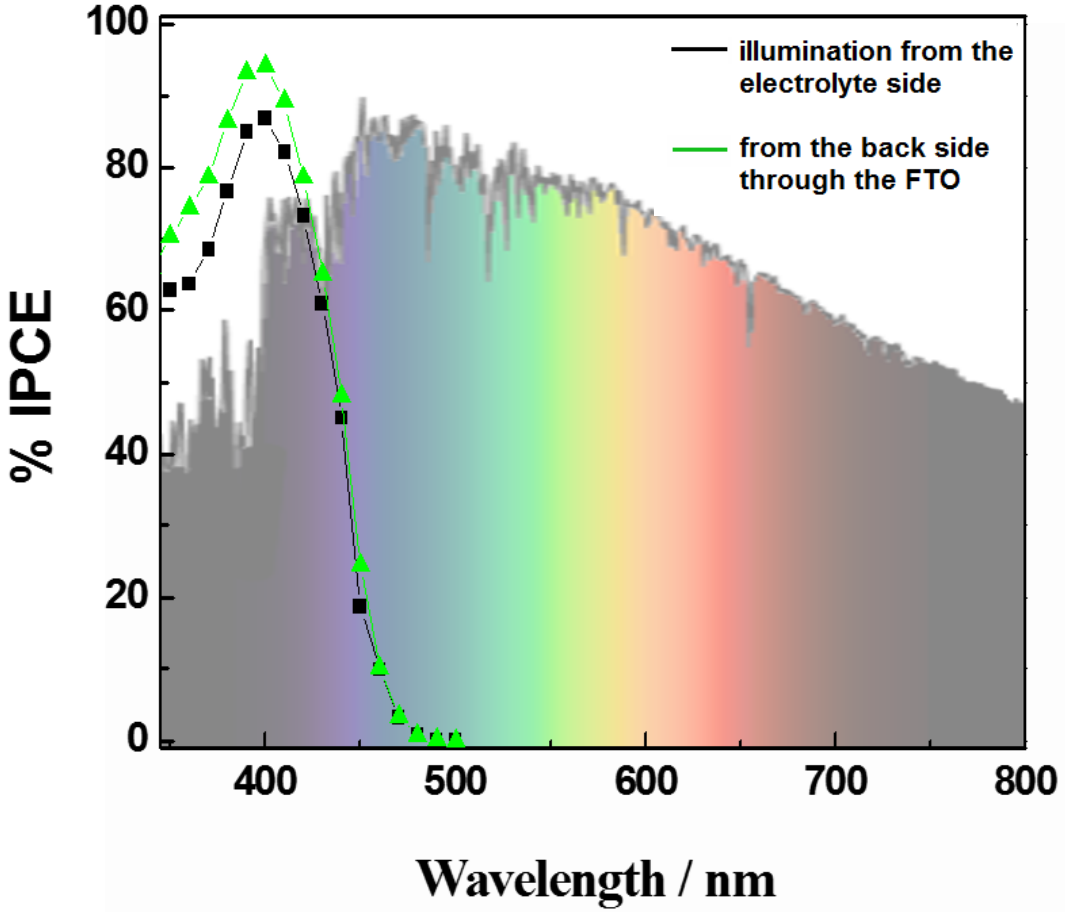
Cathodic compartment

Pd cathode: $2e^- + 2H^+ \rightarrow 2H_{abs}$ (Pd)

The use of a hydride cathode avoids mixing of gases formed in the cell. The amount of formed hydrogen is subsequently determined by discharging the palladium sheet cathode.

Collection of hydrogen in the form of a hydride opens, more generally, the prospect of subsequently using such materials as anodes in batteries employing oxygen reduction cathodes.

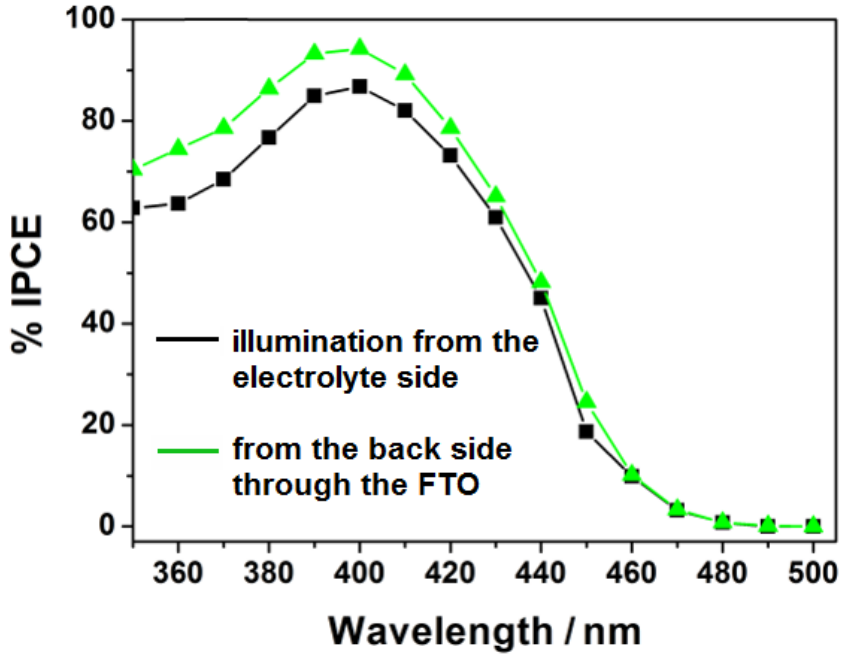
Incident photon-to-current conversion efficiencies



$$WO_3 + h\nu \rightarrow e^-_{(CB)} + h^+_{(VB)}$$

$$H_2O + 2\,h^+ \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+$$

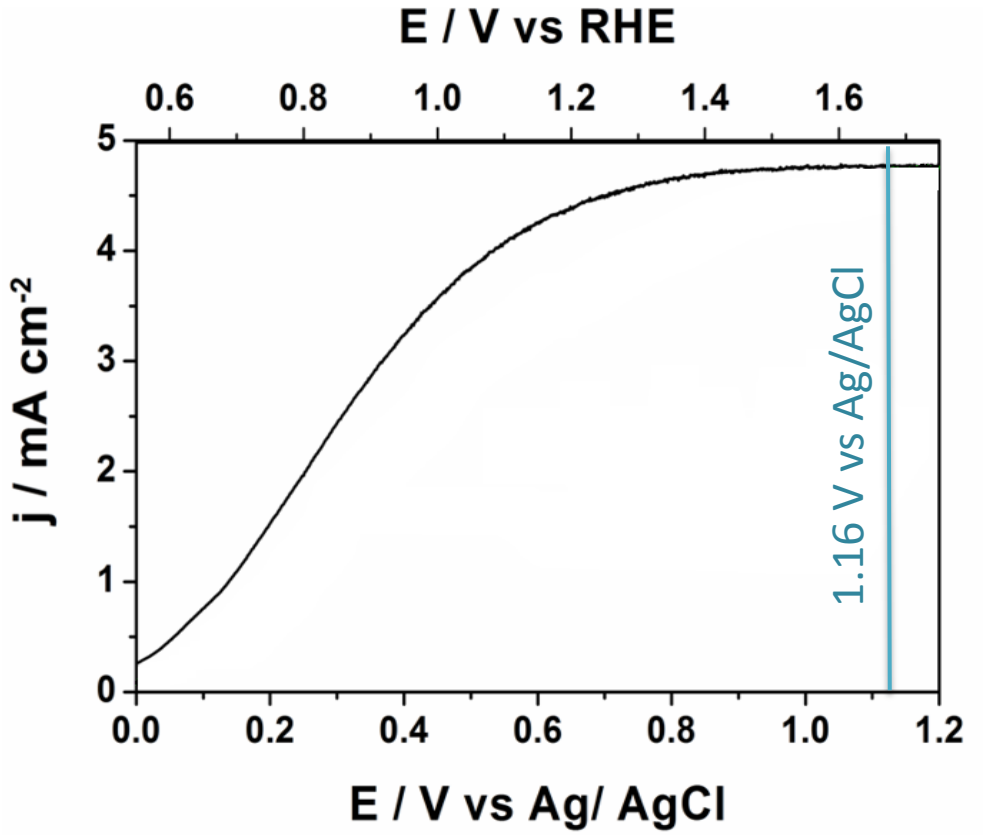
$$2Cl^- + 2h^+ \rightarrow Cl_2$$



3 µm-thick WO_3 electrode in synthetic seawater.

To be noted is the quantum efficiency of 90% attained at 400 nm.

Photoelectrochemical performance



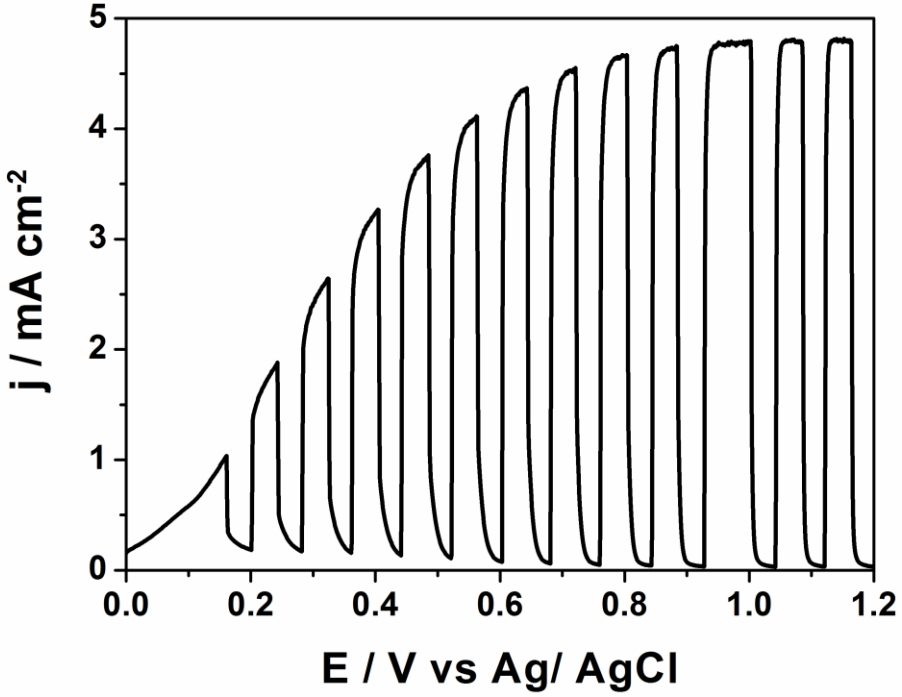


Photo-anodic current vs potential (j-E) plots for a ~ 3 µm-thick WO_3 electrode recorded in synthetic seawater under AM 1.5G (100 mW cm^{-2}).

The photocurrent of 4.5 mA cm^{-2} is attained *ca* 0.5 V below thermodynamic potential of Cl_2 evolution.

The sunlight-driven photoelectrochemical seawater splitting devices, operating on-site, might be particularly well suited to the remote places where relatively small amounts of chlorine/hypochlorite are required for a variety of vital disinfecting purposes including purification of drinking water and where seawater and sunlight are abundant.

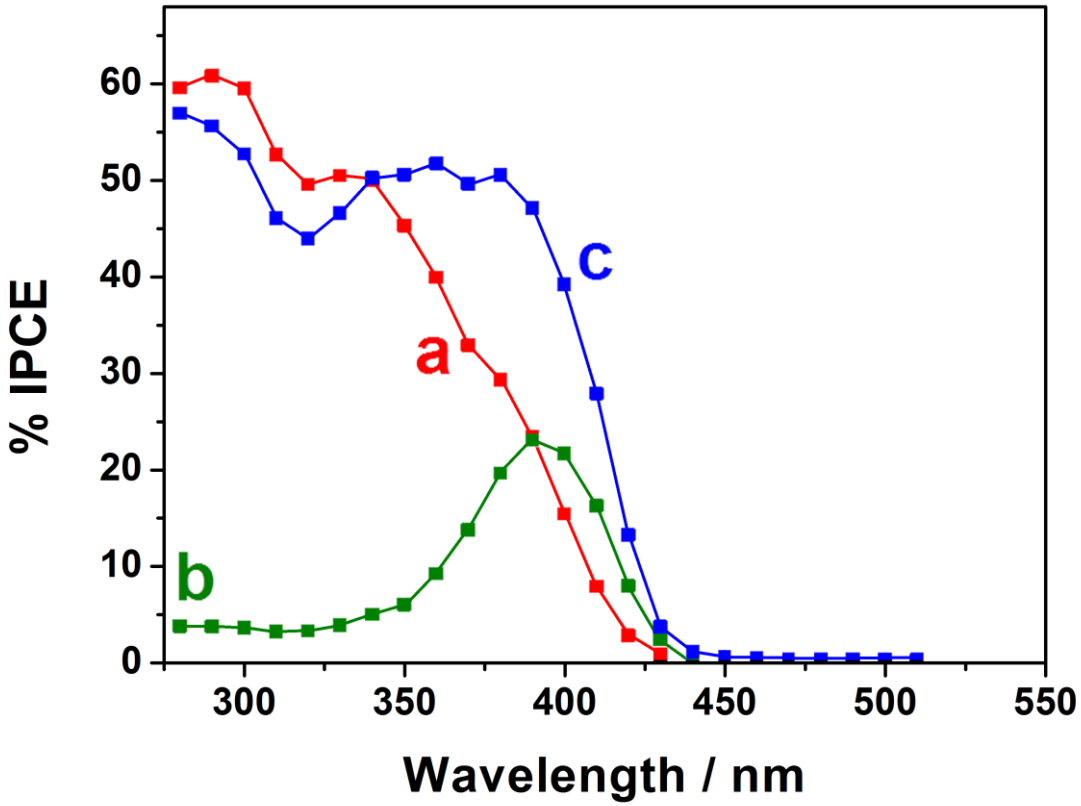
Another recent work shows activation to visible light of non-stoechiometric rutile-based TiO_2-x films formed by high-temperature oxidation of titanium metal. Removal of surface states leads to a large increase of sunlight-driven water oxidation photocurrents.

Activation of rutile TiO_2 film electrodes to photoelectrochemical water splitting under visible light.

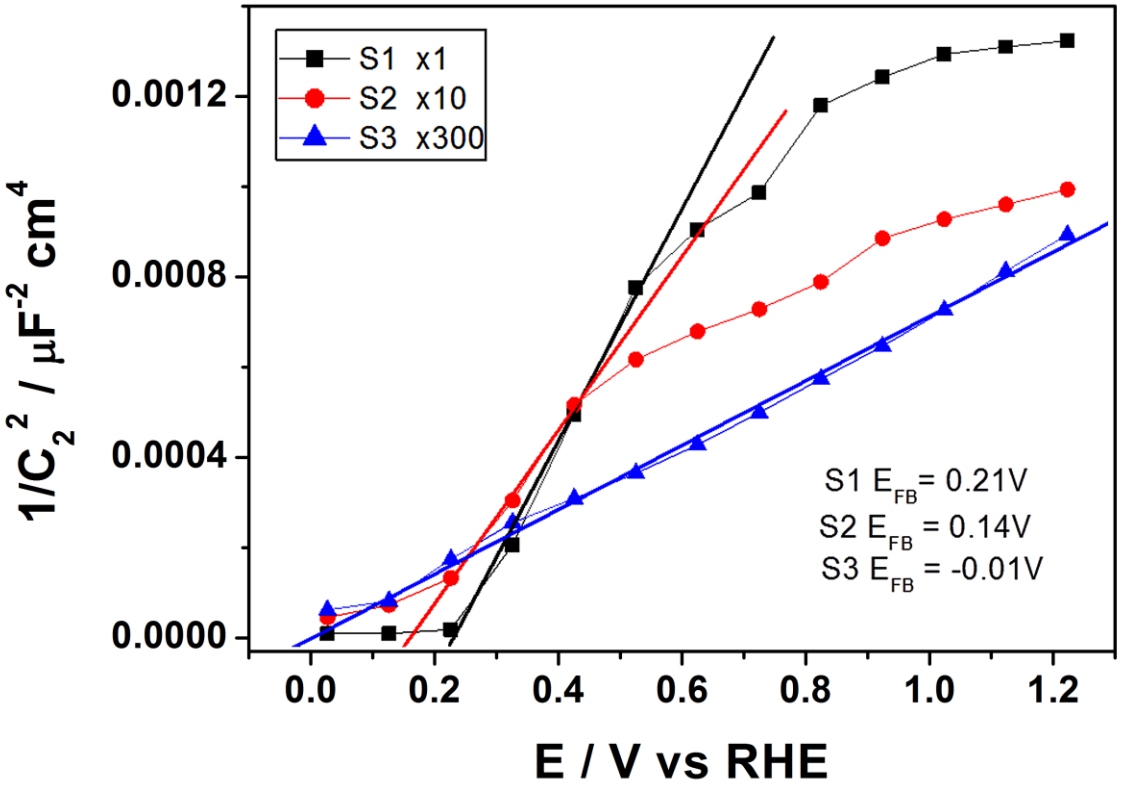
P. J. Barczuk, K. Noworyta, M. Dolata, K. Jakubow-Piotrowska, J. Augustynski

Sol. Energy Mater. Sol. Cells, **2020**, *208*, 110424.

Photoelectrochemical characterization



Spectral photoresponses of electrodes prepared by Ti oxidation in oxygen flow at 600 °C (a), 850°C (b) and 850°C and subsequently etched for 45 min in boiling KHC_2O_4 (c). Curves recorded in 1M $HClO_4$.



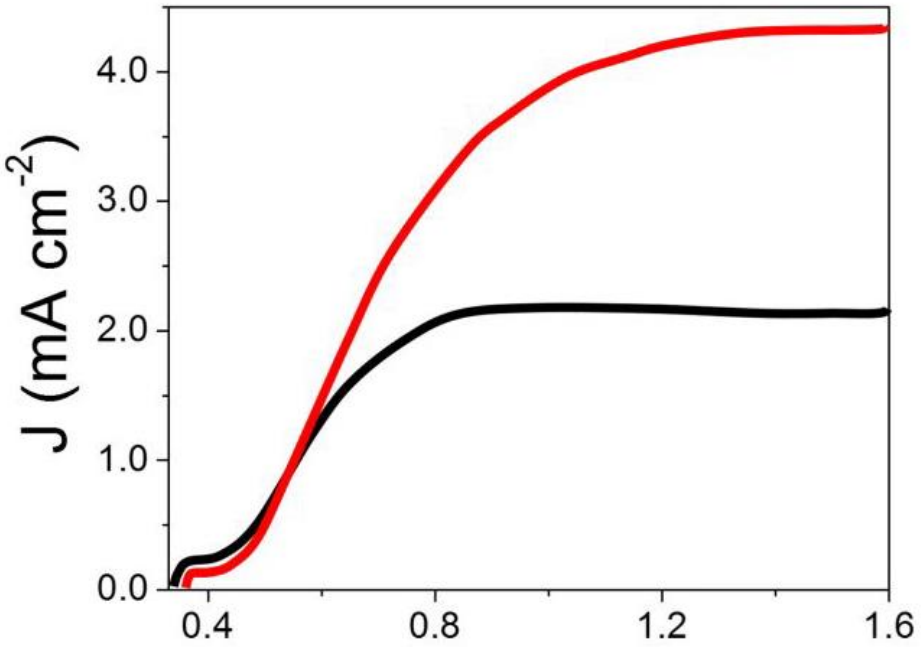
Mott-Schottky plots for the rutile electrodes prepared by Ti oxidation at 600°C (S1), 850°C (S2) and at 850°C and subsequently etched in KHC_2O_4 (S3).

In that work we identified nano-hetero structure formed at the interface between a thin WO_3 film and the SnO_2 substrate leading to very large enhancement of optical absorption and water splitting photocurrents of the photoanode.

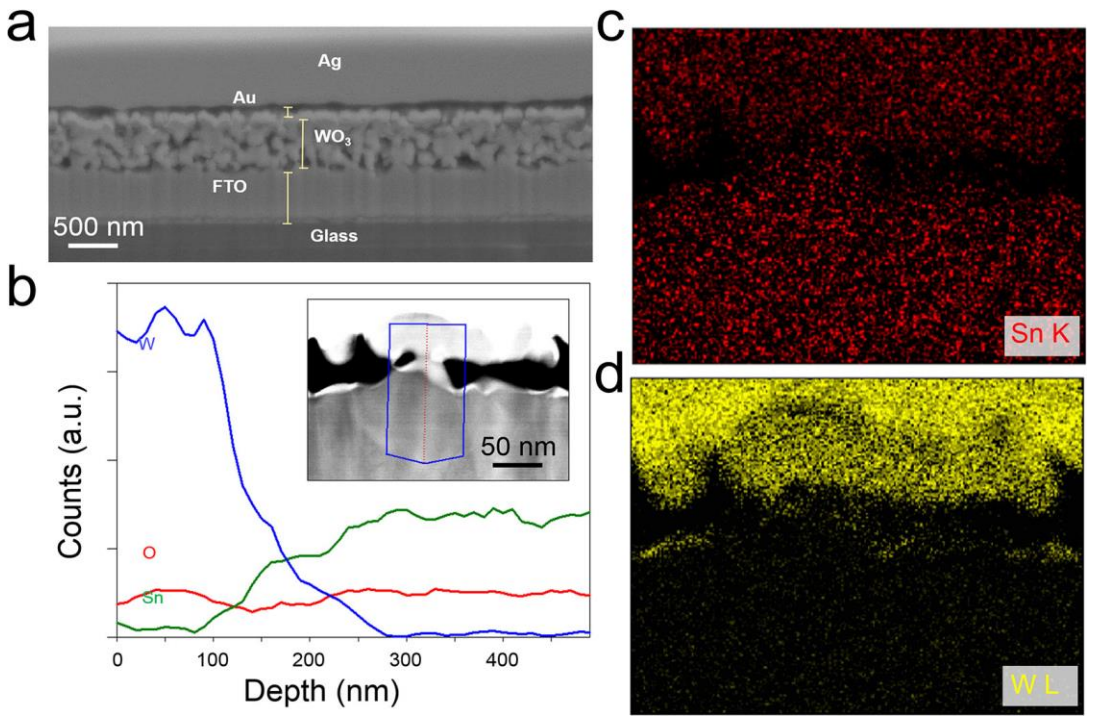
Enhanced Photocatalytic Water Splitting on Very Thin WO_3 Films Activated by High-Temperature Annealing

A. Jelinska, K. Bienkowski, M. Jadwiszczak, M. Pisarek, M. Strawski, D. Kurzydlowski, R. Solarska, J. Augustynski

ACS Catalysis, **2018***, 8*, 10573.



PEC water oxidation currents plotted against applied potential for WO_3 electrodes annealed at 550°C (black curves) and after further annealing for 36 min. at 670°C (red curves) for a 1.2 µm-thick film. Measurements were performed in a 1 M CH_3SO_3H supporting electrolyte under simulated AM 1.5G (100 mW cm^{-2}) sunlight.



STEM-EDX analyses of the cross section of approximately 0.25 µm thick WO3 film after annealing at 670°C. Panel (a) shows a SEM image of the analyzed cross section, panel (b) displays EDX line scans for W, Sn and O corresponding to the red line within the delineated fragment in the STEM image showed as an inset. Included are also in panels (c) and (d) maps for elemental Sn and W.

Laboratory of Photoelectrochemistry and Solar Energy Conversion

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Michael Greatzel - Laboratory of Photonics; Ecole Polytechnique Fédérale de Lausanne;

Lionel Vayssieres - International Research Center for Renewable Energy; IRCRE Xi'an Jiaotong University (China).

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