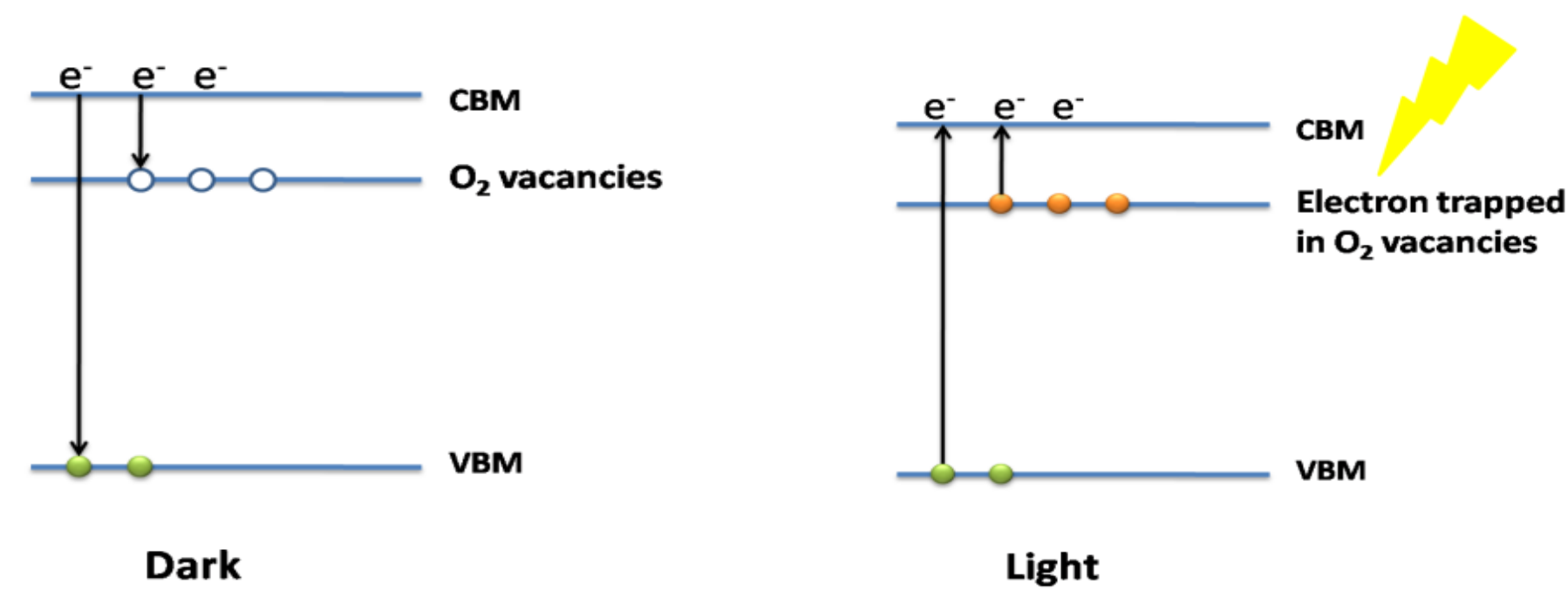


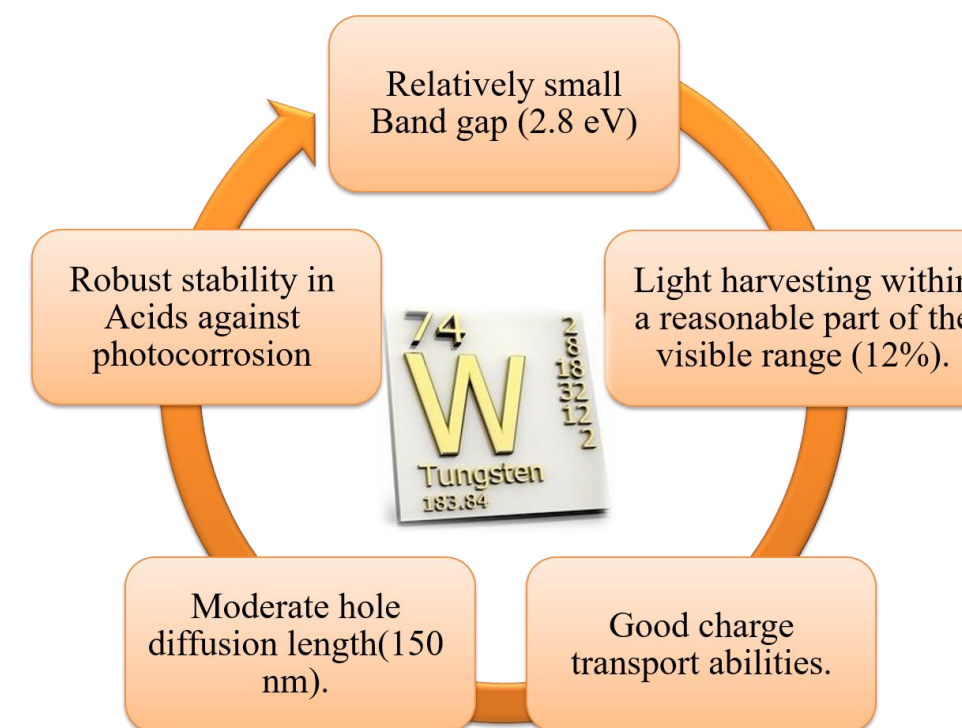
## Introduction

It is widely accepted that oxygen vacancies are the major contributors of photocurrent in n-type metal oxide semiconductors. These point defects form inter-bandgap states below the conduction band minimum (CBM), providing extra charge carriers under illumination. In addition, because of electron trapping processes occurring within such shallow defect states, their net effect is to increase the photoelectrons' lifetime, which is very beneficial upon the use of such materials in solar water splitting. The increased lifetime would allow more time for photogenerated holes in the valence band to move towards the electrode/electrolyte interface and take part in catalysis reactions, resulting in increased photocurrents.



Emerging recently as promising photoanodes for water splitting, tungsten oxides have been thoroughly studied from that perspective owing to the stability of a number of oxygen-rich/deficient forms, including WO<sub>3</sub>, WO<sub>2.9</sub>, WO<sub>2.8</sub>, WO<sub>2.72</sub>, and WO<sub>2.5</sub>.

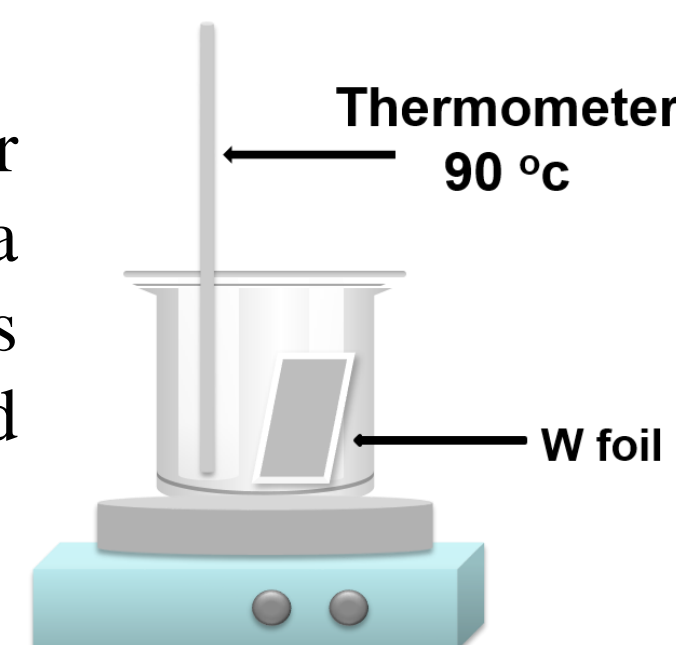
In fact, the occurrence of undesired surface reactions, such as the formation and dissolution of peroxy-species on the surface of tungsten oxides, has been shown to decrease with oxygen deficiency making its presence vital to the stability of such electrodes as photoanodes in water splitting.



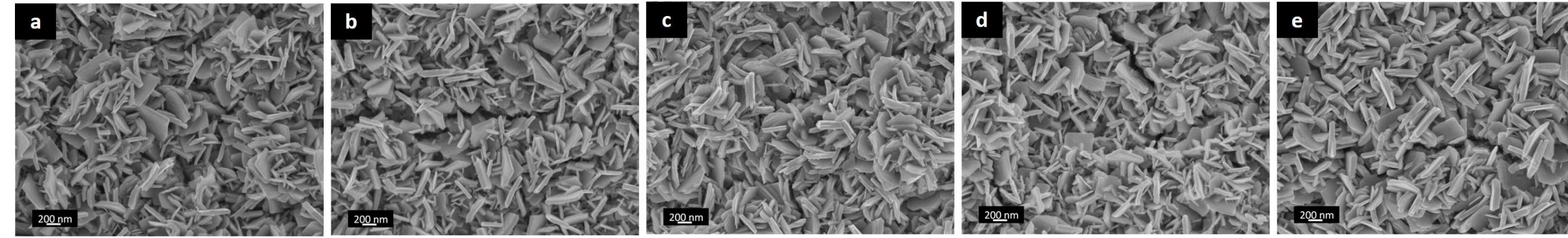
## Methodology

In order to produce WO<sub>3</sub> nanoflake photoanodes, W foils were placed perpendicularly in aqueous solutions containing 1 M HNO<sub>3</sub> and heated up to 90 °C for 2 h.

The as-prepared samples were annealed under different gases (air, H<sub>2</sub> and O<sub>2</sub>) for 2 h at 450 °C with a heating rate of 3 °C min<sup>-1</sup>. Additional treatments included annealing in air under the aforementioned conditions, then in O<sub>2</sub> or H<sub>2</sub> for 30 min at 350 °C.



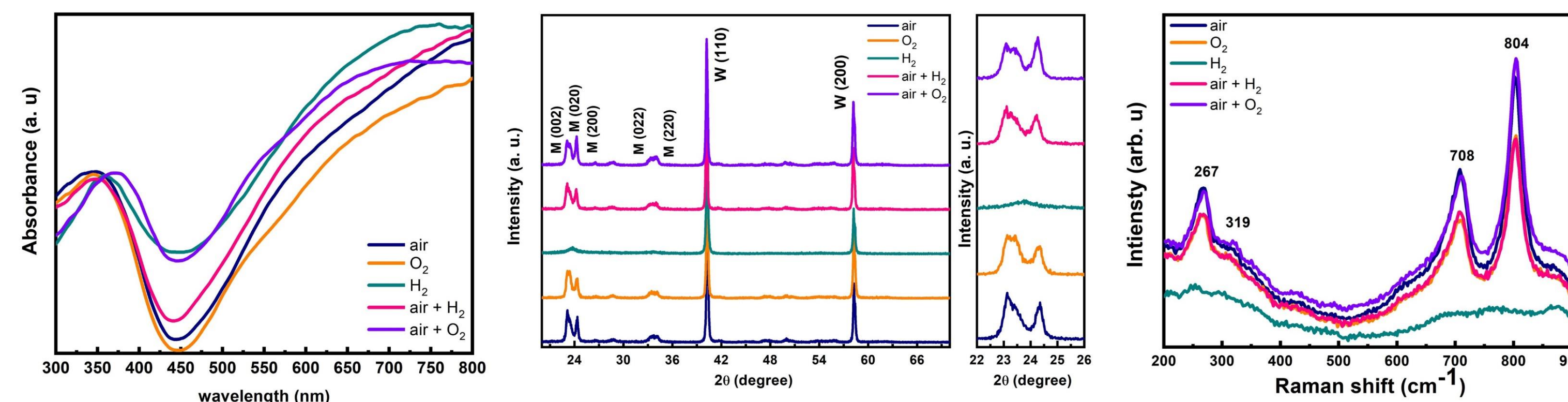
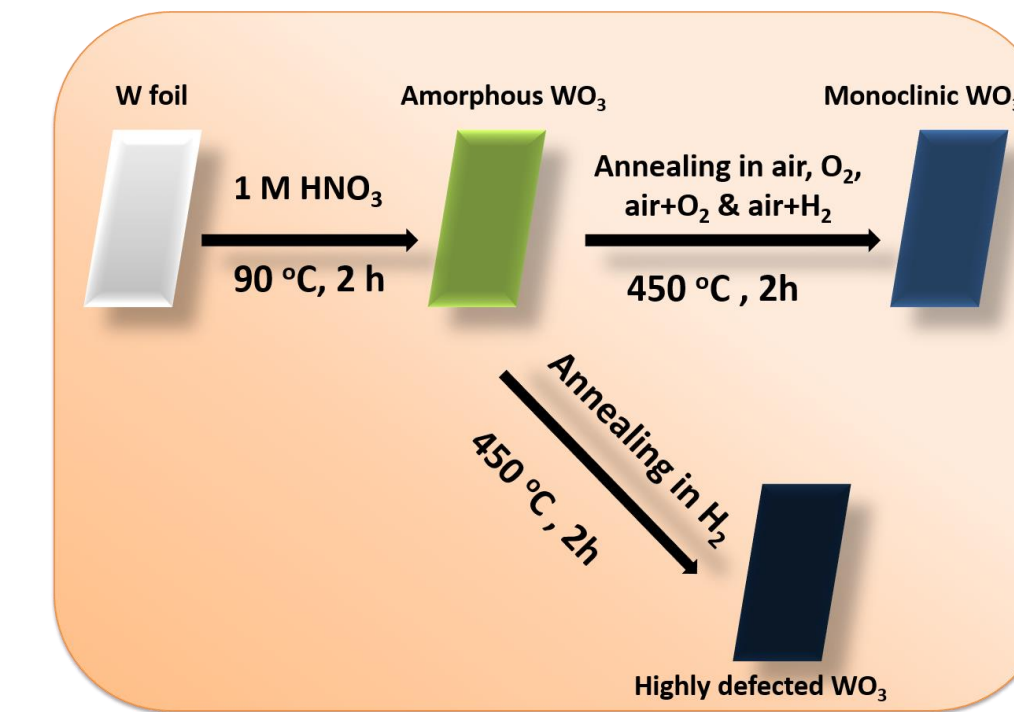
## Morphological, optical and structural characterization



FESEM top view images of Tungsten oxide nanoflakes films annealed in (a) air, (b) Oxygen, (c) Hydrogen, (d) air followed by Oxygen, and (e) air followed by Hydrogen.

The thermoacidic treatment resulted in the formation of consistent nanoflakes with dimensions of about 350 x 550 x 55 nm<sup>3</sup>. Annealing the nanoflakes at 450 °C under streams of different gases conserved their structure and dimensions. Note that the thickness of the nanoflakes is within the proximity of the minority carrier diffusion length (150 nm).

The as-prepared sample exhibited a greenish color. Annealing under different atmospheres resulted in a color change to dark blue, with the samples annealed in a pure H<sub>2</sub> atmosphere showing the darkest appearance. This color variation upon annealing could be ascribed to the possible modification in the crystal structure. In particular, blue color indicates the presence of oxygen vacancies and the formation of sub-stoichiometric WO<sub>3-x</sub>.



(a) UV-Vis absorbance spectra for samples annealed under different atmospheres. (b) The respective XRD patterns and (c) Raman spectra of the samples.

- All DRS spectra showed similar absorption edges around 450 nm, as well as absorption tails in the visible and near-IR regions, ascribed to absorption of electrons in inter-band states, such as O<sub>2</sub> vacancies.
- The XRD showed diffraction peaks indexed to the monoclinic phase of WO<sub>3</sub>, which is the most stable and photoactive phase of WO<sub>3</sub> except for the one annealed under only a stream of H<sub>2</sub>.
- As grain growth indicates enhanced crystallinity, it can be inferred that dominance of a stoichiometric monoclinic phase in the samples showed the following order: Air + O<sub>2</sub> > O<sub>2</sub> > Air + H<sub>2</sub> > Air > H<sub>2</sub>.

- Raman spectra confirmed the presence of the monoclinic phase with the characteristic peaks corresponding to vibrational modes of tungstates centered at 267, 708 and 804 cm<sup>-1</sup> for all samples except that annealed only under H<sub>2</sub> stream.

Sample	FWHM [°2θ]	2θ (°)	D (nm)
Air	0.2880	23.1134	28.28
O <sub>2</sub>	0.1968	23.4770	41.25
Air + O <sub>2</sub>	0.1574	24.2704	51.6
Air + H <sub>2</sub>	0.2362	23.0498	34.31
H <sub>2</sub>	0.7872	23.6934	10.31

## Electrochemical characterization

The performance of the samples annealed in air was superior to that of the other electrodes with a photocurrent density reaching 1.33 mA cm<sup>-2</sup> at 1.2 V<sub>SCE</sub>.

To analyse the nature of defect states within the samples, a current density shift term is defined (*C*) measuring the ratio of the current density of a sample annealed under any gas stream to that of a sample annealed in air, i.e.

$$C = \frac{J_{Gas}}{J_{Air}}$$

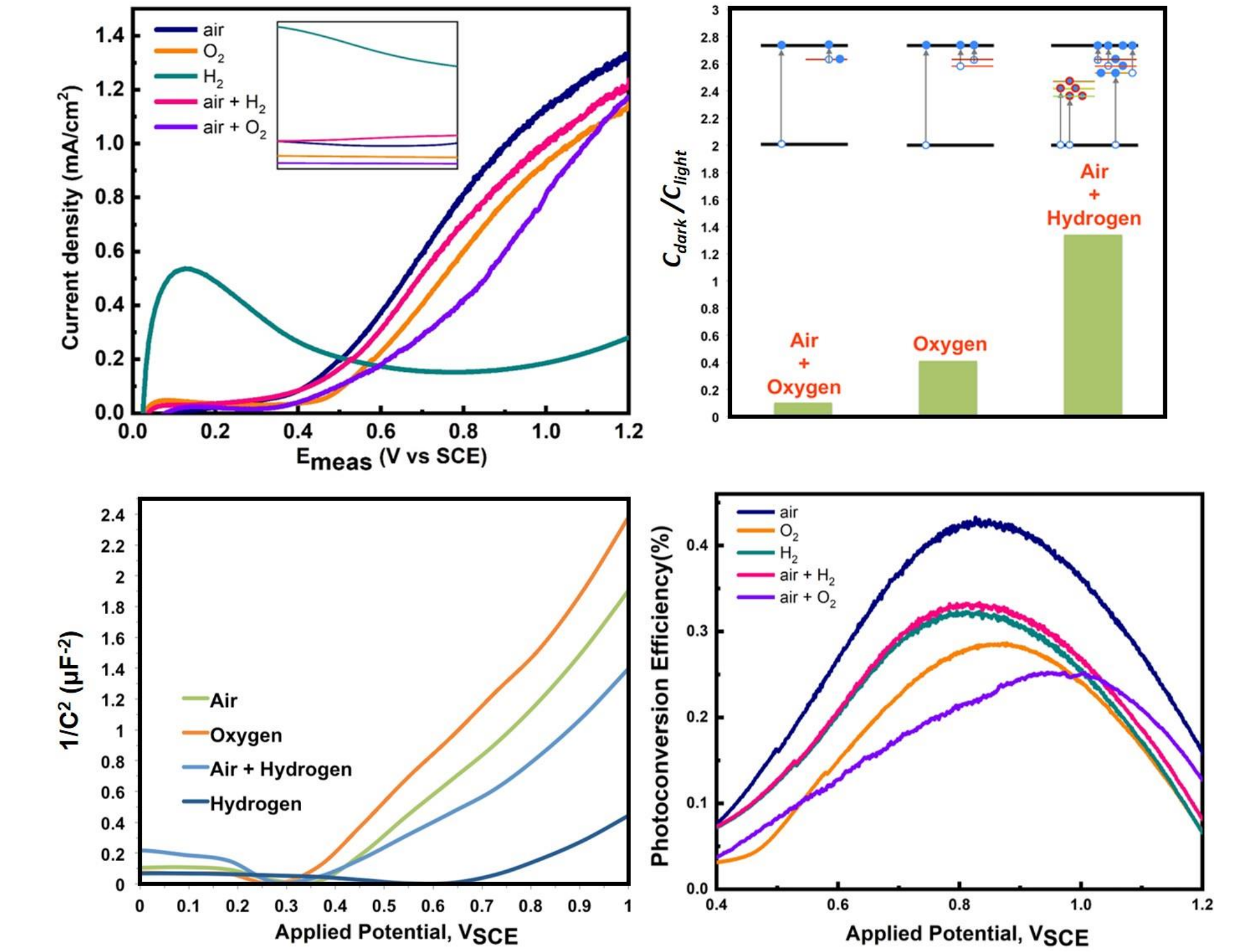
Based upon that term, a defect sensitivity factor is proposed as follows:

$$\frac{C_{dark}}{C_{light}}$$

Where *C<sub>dark</sub>* and *C<sub>light</sub>* are the corresponding ratios in the dark and under illumination, respectively. This factor illustrates the decrease in dark current versus the decrease in photocurrent in any given annealing conditions.

Based upon *J-V* data, the following can be inferred on the arrangement of the samples according to the abundance of defect states: H<sub>2</sub>>Air+H<sub>2</sub>>Air>O<sub>2</sub>>Air+O<sub>2</sub>, well agreeing with structural analysis of the samples.

The analysis of photocurrent density data was also confirmed using Mott-Schottky analysis



(a) *J-V* plots of illuminated tungstate nanoflakes. Inset shows plots in the dark. (b) Defect sensitivity factors for tungstate nanoflakes annealed under different conditions with a schematic showing the nature of defects in each sample. (c) Mott-Schottky plots of the tungstate nanoflakes and (d) the corresponding Photoconversion efficiencies.

Sample	Photocurrent density (mA/cm <sup>2</sup> )	V <sub>FB</sub> (V)	N <sub>D</sub> x 10 <sup>22</sup> (cm <sup>-3</sup> )	Max Photoconversion efficiency
Air	1.30	0.384	0.91	0.430 at 0.83 V
O <sub>2</sub>	1.14	0.324	0.82	0.285 at 0.85 V
H <sub>2</sub>	0.28	0.635	2.33	0.320 at 0.80 V
Air + H <sub>2</sub>	1.24	0.387	1.27	0.330 at 0.80 V
Air + O <sub>2</sub>	1.18	-	-	0.250 at 0.92 V

## Summary

The study demonstrates a facile electrochemical method to detect the nature of Oxygen vacancy defect states inside tungstate nanoflake arrays. Annealing under different gas streams was used to engineer the defects inside the photoanodes. UV-Vis spectra and XRD patterns confirmed the presence of defected tungstate structures in all samples, with the samples annealed in air followed by a 30- minute O<sub>2</sub> treatment showing the most stoichiometric monoclinic structures. *J-V* plots in the dark and under illumination were used to indicate whether Oxygen vacancy states are deep or shallow in nature in all samples. It was concluded that defects inside the material increase in the following order of annealing gases: Air + O<sub>2</sub> < O<sub>2</sub> < Air < Air + H<sub>2</sub> < H<sub>2</sub>. This order was confirmed using donor density values extracted from Mott-Schottky analysis. Also, flat band potentials were used to confirm the fact that treating tungstate nanoflakes with H<sub>2</sub> induced defect states inside the material of both types, with deep states increasing at a greater rate. The enhanced stoichiometry of the samples treated with O<sub>2</sub> after air annealing was confirmed using Photocurrent transients.

## References

1. A. M. Mohamed, S. A. Shaban, H. A. El Sayed, B. E. El-Anadouli and N. K. Allam, *Int J. Hydrogen Energy*, 2016, 41, 866-872.
2. A.M. Mohamed, A. W. Amer, S. Y. AlQaradawi, N. K. Allam, *Phys. Chem. Chem. Phys.*, 2016, 18, 22217-22223.