Energy Materials

Supplementary Materials

Exploring the interplay of Ti–Sn co-doping in photoelectrochemical water splitting of hematite nanowires

Francisco Javier Fernández-Alonso[1,2,3], Paula Quiterio[4], Rui Vilarinho[4], João P. Araújo[4], Adélio Mendes[5], Miguel Manso-Silván[1,2,3], Vicente Torres-Costa[1,2], Arlete Apolinario[4], Célia Tavares de Sousa[1,2,3]

[1]Departamento de Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid 28049, Spain.
[2]Instituto "Nicolás Cabrera", Facultad de Ciencias, Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid 28049, Spain.
[3]Centro de Microanálisis de Materiales, Universidad Autónoma de Madrid, Madrid 28049, Spain.
[4]IFIMUP - Institute of Physics for Advanced Materials, Nanotechnology and Photonics of University of Porto, Departamento de Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Porto 4169-007, Portugal.
[5]LEPABE - Faculdade de Engenharia, Universidade do Porto, Porto 4200-465, Portugal.

[*]**Correspondence to:** Dr. Célia Tavares de Sousa, Departamento de Física Aplicada, Facultad de Ciencias, Calle Francisco Tomás y Valiente 7, M12-104, Madrid 28049, Spain. E-mail: celia.tsousa@uam.es

RELATIVE INTENSITY OF THE XRD (101) PEAK

Supplementary Table 1. Intensity of the diffraction peak (110), in relation to the intensity of the diffraction peak (104) for the different samples

Sample	I_{110}/I_{104}
Reference (JCPDS 33-0664)	1.34
600 ºC	5.7
Ti-600 ºC	1.5
800 ºC	20.9
Ti-800 ºC	2.8

CRYSTALLITE SIZE DETERMINATION

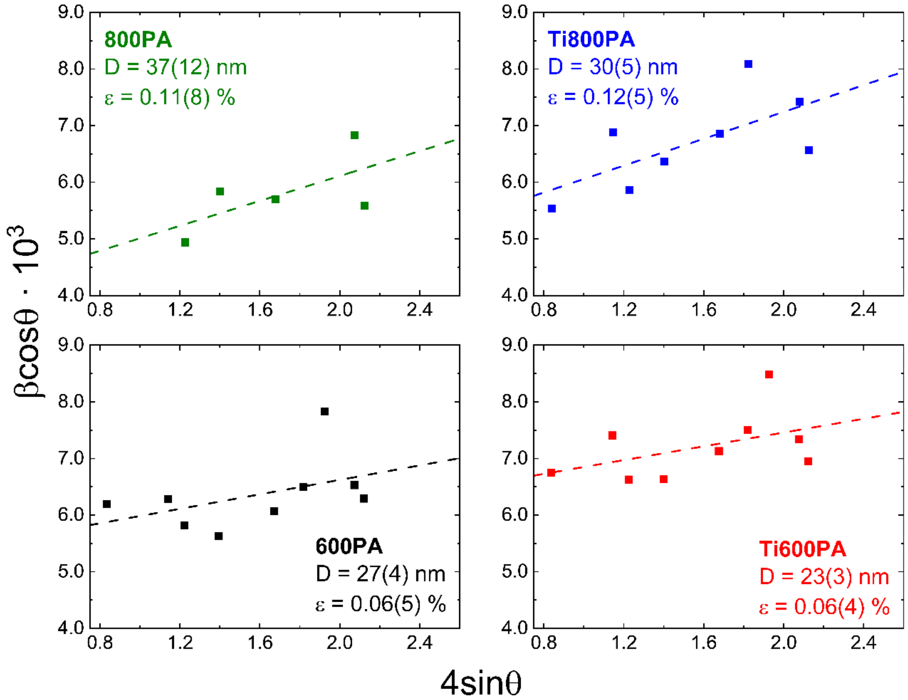
From the X-ray diffractograms the crystallite size *D* and inhomogeneous microstrain ϵ can be estimated by applying the Williamson-Hall method [1]. According to this model, from the width at half height β of the different peaks, *D* and ϵ can be estimated. The total width at half height is given by **Supplementary Equation 1**, where λ is the wavelength of the incident X-rays, and *K* corresponds to the Scherrer constant.

$$\beta = \frac{K\lambda}{D\cos\theta} + 4\epsilon\tan\theta \qquad (S1)$$

Therefore, by multiplying both terms by cosθ, **Supplementary Equation 2** is obtained:

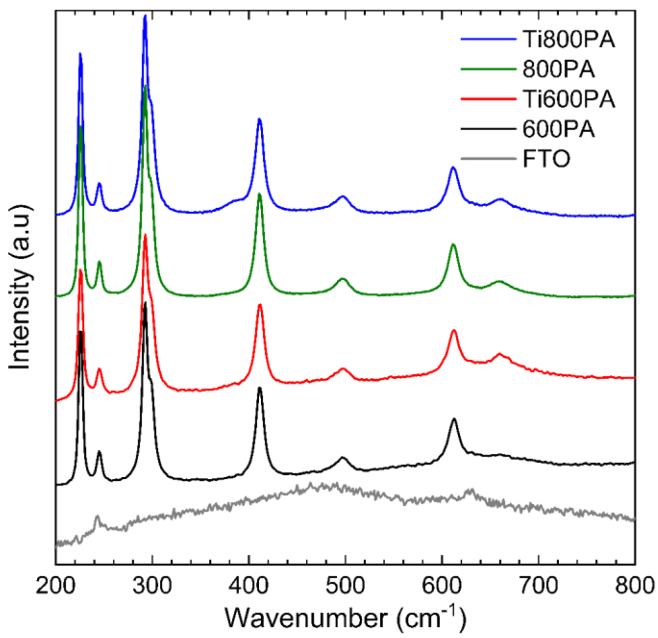
$$\beta\cos\theta = \frac{K\lambda}{D} + 4\epsilon\sin\theta \qquad (S2)$$

Therefore, by plotting βcos θ as a function of 4sin θ, ϵ can be estimated from the slope, and *D* from the y-axis intercept. Crystallites are generally considered to have cubic symmetry, in which: $K = 2\left(\frac{ln2}{\pi}\right)^{1/2} \approx 0.9394$. **Supplementary Figure 1** shows the plot of βcos θ as a function of 4 sin θ, for different photoanodes.



Supplementary Figure 1. Determination of D and ϵ applying the Williamson – Hall model, for the undoped and Ti-doped hematite NWs, subjected to one-step and two-step annealing processes.

RAMAN SPECTROSCOPY

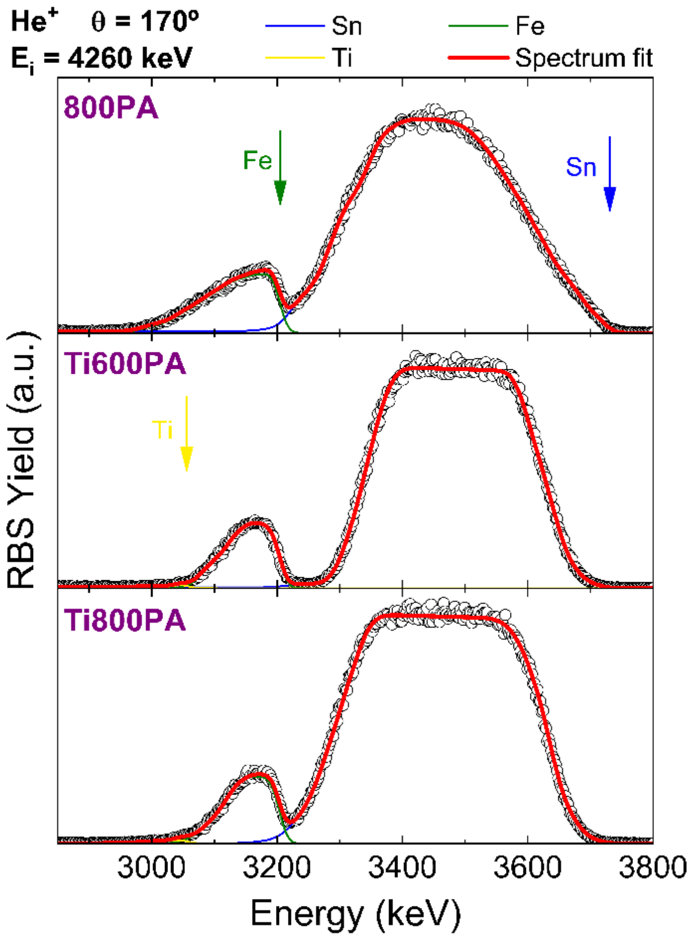


Supplementary Figure 2. Raman spectra of undoped and Ti-doped hematite photoanodes.

Supplementary Table 2. Full width at half-maximum (FWHM) of Raman peaks for hematite NWs synthetized with and without Ti-dopant

	FWHM					
Sample	(225 cm^{-1})	(245 cm^{-1})	(293 cm^{-1})	(410 cm^{-1})	(611 cm^{-1})	(660 cm^{-1})
600PA	4.6±0.1	6.0±0.5	6.1±0.1	9.7±0.1	13.2±0.2	87.3±4.7
Ti600PA	5.3±0.1	6.7±0.5	6.8±0.1	10.4±0.1	15.2±0.3	51.8±1.5
800PA	4.7±0.1	5.4±0.6	6.5±0.1	9.8±0.1	13.8±0.1	35.7±0.5
Ti800PA	4.9±0.1	6.1±0.5	6.6±0.1	10.6±0.1	15.0±0.2	40.9±1.0

RUTHERFORD BACKSCATTERING ANALYSIS SPECTRA



Supplementary Figure 3. RBS spectra collected from the 800 ºC, Ti-600 ºC and Ti-800 ºC photoanodes. The contribution of each element to the total spectrum is highlighted. The arrows indicate the theoretical energy of the highest energy barrier if the element was present at the surface.

REFERENCES

1 Williamson GK, Hall WH. X-ray line broadening from filed aluminium and wolfram. *Acta Metallurgica* 1953;1:22–31. [DOI: 10.1016/0001-6160(53)90006-6]