

## **Multihierarchical electrodes based on titanate nanotubes and zinc oxide nanorods for photoelectrochemical water splitting**

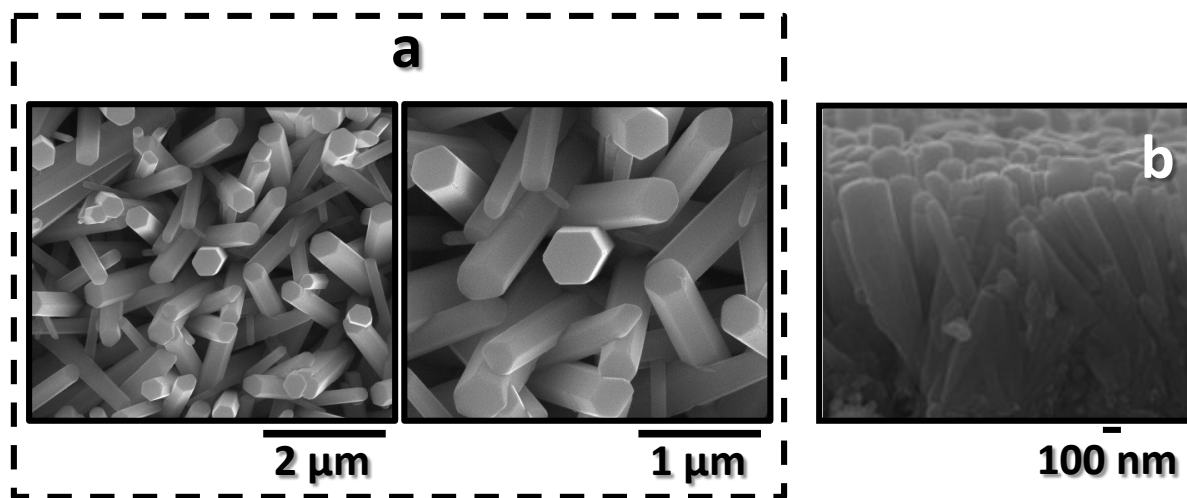
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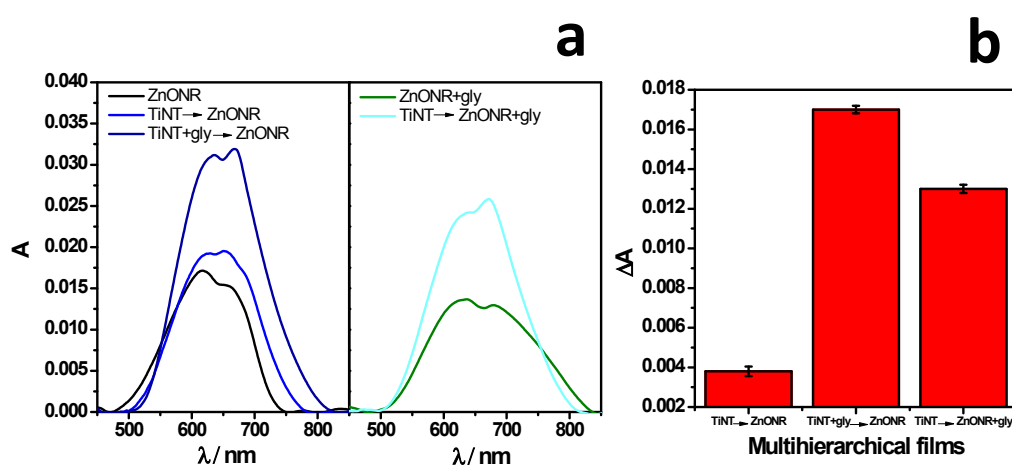
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Figure S1 show the SEM images of ZnONR+gly film obtained at different magnifications. Cross section SEM image of the ZnONR film is also presented, Figure S1b, showing the vertical alignment of the rods.



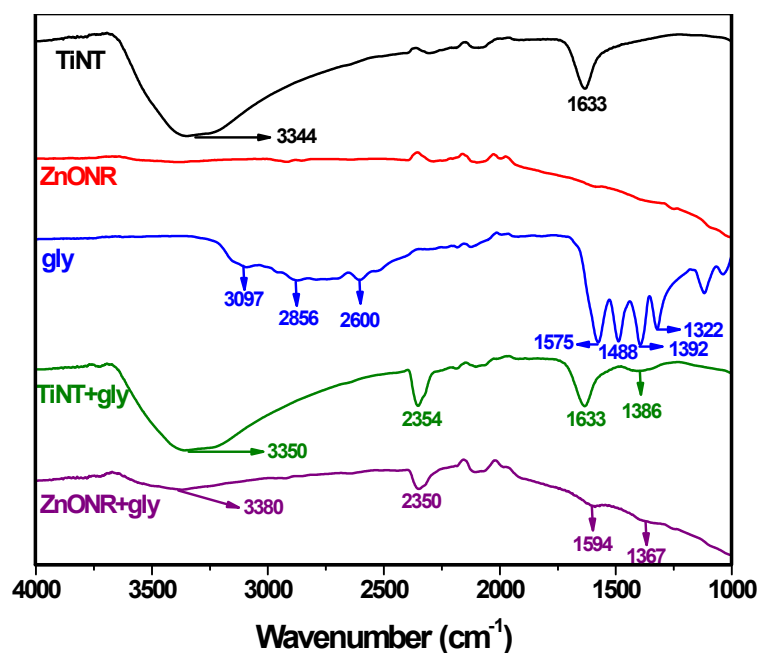
**Figure S1.** (a) SEM images of ZnONR+gly film. (b) Cross section image of ZnONR film.

TiNT decorated ZnONRs films were soaked in MB solutions for 8h, aiming to create a monolayer of the dye on the surface of TiNT. Using a UV-Vis spectrometer, the absorbance spectra of all samples were recorded and the absorption of the dye was measured at its maximum absorption of 654 nm. Figure S2a show the absorbance spectra of the methylene blue decorated ZnONR, ZnONR+gly, TiNT→ZnONR, TiNT+gly→ZnONR and TiNT→ZnONR+gly films. The difference in absorbance of the dye coated multihierarchical films and the non-decorated ZnONR and ZnONR+gly films ( $\Delta A$ ) was calculated<sup>1</sup>, Figure S2b; these results were associated to the amount of TiNT present in the multihierarchical electrodes.



**Figure S2.** (a) UV-Vis spectra of dye coated multihierarchical electrodes and non-decorated ZnONR and ZnONR+gly films; (b) Difference in the absorbance of decorated and non-decorated films  $\Delta A$ .

FTIR spectra of pure TiNT, ZnONRs and glycine and the spectra of TiNT+gly and ZnONR+gly were obtained, Figure S3, aiming to prove the modification of the nanotubes and nanorods with the glycine.

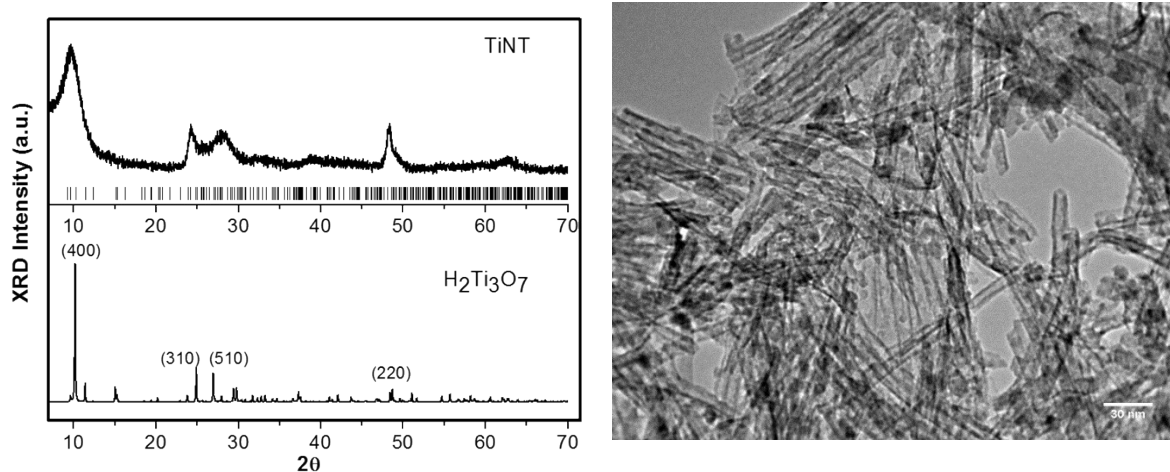


**Figure S3.** Infrared spectra of TiNT, ZnONR, gly, TiNT+gly and ZnONR+gly

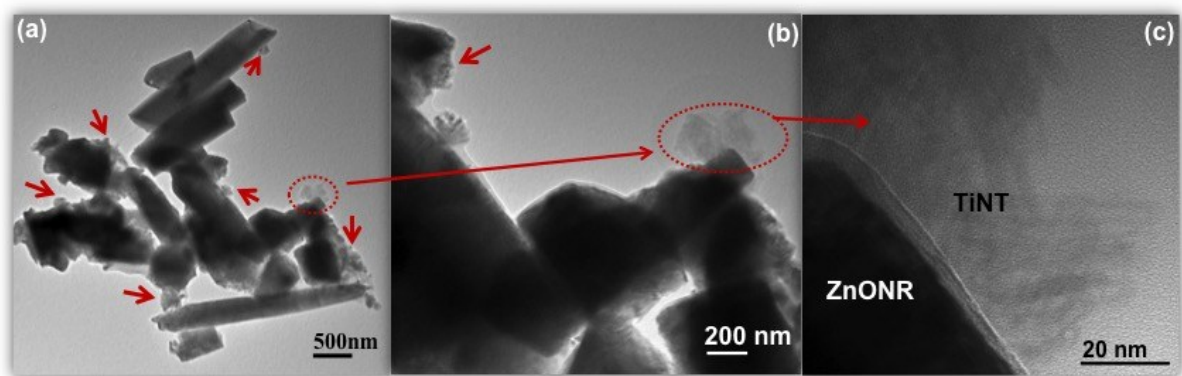
The spectrum of TiNT exhibit a large and intense band around  $3344\text{ cm}^{-1}$  which is ascribed to the  $\nu(\text{O-H})$  of  $\text{Ti-O-H}$  <sup>2</sup> and a band in around  $1633$  ascribed to  $\delta(\text{O-H})$  <sup>3, 4</sup>. The spectrum of ZnONR does not exhibit any intense peak in the selected region. In the glycine spectrum is possible to some overlap bands around  $3097$ ,  $2856$  and  $2600\text{ cm}^{-1}$  that can be ascribed to  $\nu(\text{N-H})$ ,  $\nu_{\text{a}}(\text{C-H})$  and  $\nu_{\text{s}}(\text{C-H})$  respectively. The band in around  $1575\text{ cm}^{-1}$  can be ascribed to  $\nu_{\text{a}}(\text{COO}^-)$  and the band in  $1392\text{ cm}^{-1}$  can be to the symmetric stretching  $\nu_{\text{s}}(\text{COO}^-)$ . Finally the bands in  $1488$  and  $1322\text{ cm}^{-1}$  are ascribed to  $\delta(\text{N-H})$  and  $\delta(\text{C-H})$  respectively<sup>5</sup>.

When TiNT is modified with glycine the FTIR spectrum show few changes, first is possible to see a band in around  $2354\text{ cm}^{-1}$  which can be ascribed to  $\nu(\text{NH}_3^+ \text{ ion})$  <sup>5</sup>suggesting that the amino group of glycine became protonated when bonded to the TiNT. The second change is the arising of a broad band in around  $1386\text{ cm}^{-1}$ , in the same region that some bands of glycine are observed. The spectrum of ZnONR modified with glycine on the other hand show more evidence of the presence of glycine. First the broad band in around  $3380\text{ cm}^{-1}$  ascribed to  $\nu(\text{N-H})$ , the band in  $2350\text{ cm}^{-1}$  ascribed to  $\nu(\text{NH}_3^+ \text{ ion})$ , and two low intense bands in  $1594$  and  $1367\text{ cm}^{-1}$  that can be ascribed to  $\nu_{\text{a}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  respectively.

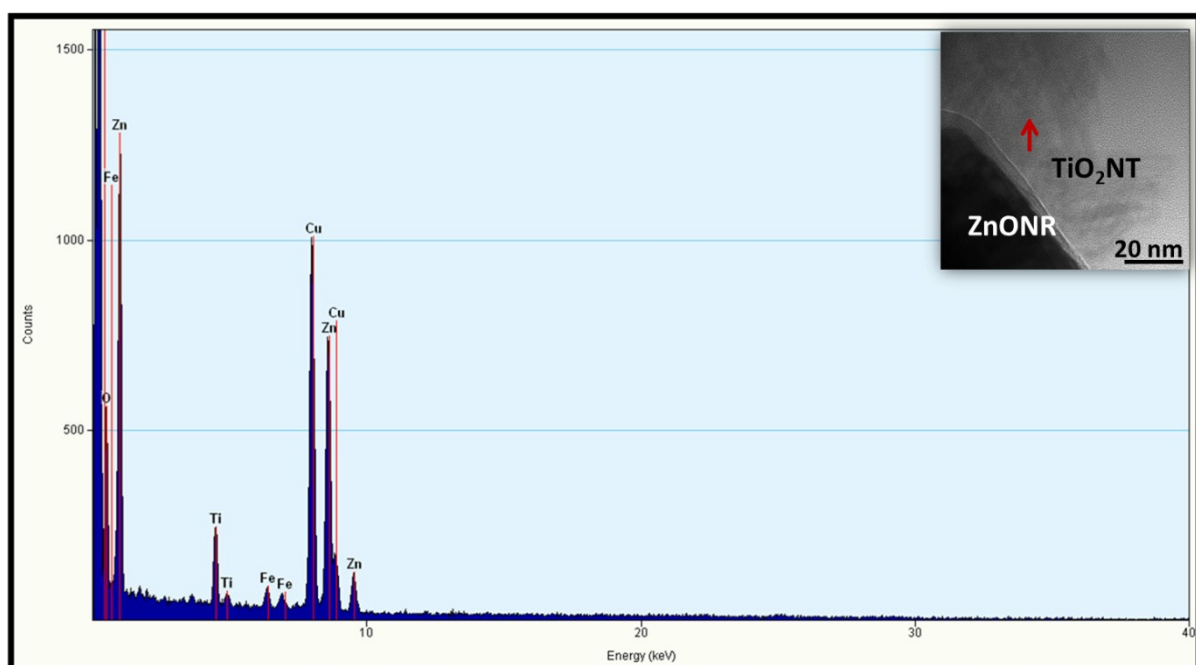
Figure S4 show XRD patterns of the titanate nanotubes used to prepare the multihierarchical electrodes, and its comparison to the XRD pattern of  $H_2Ti_3O_7$  available on ICSD. TEM image of the TiNT is also exhibited, showing the tubular shape of the nanomaterials. Although we have ascribed the TiNT XRD pattern to the  $H_2Ti_3O_7$  crystalline structure, there is a discussion in the literature regard the correct structure for these material<sup>6, 7</sup>.



**Figure S4.** Comparison of the XRD pattern of TiNTs with the calculated XRD pattern of  $H_2Ti_3O_7$  crystalline structure (ICSD245891).

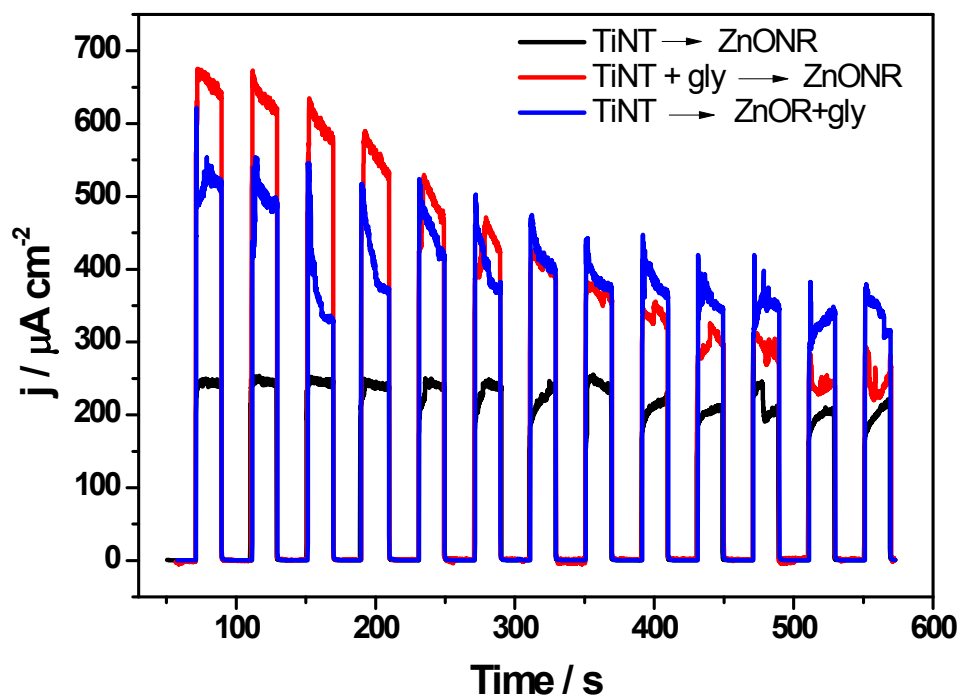


**Figure S5.** (a-c) Represent the sequence of TEM images of TiNT deposited over the ZnONR. The red arrows indicated the presence of TiNT attached at ZnONR surface.



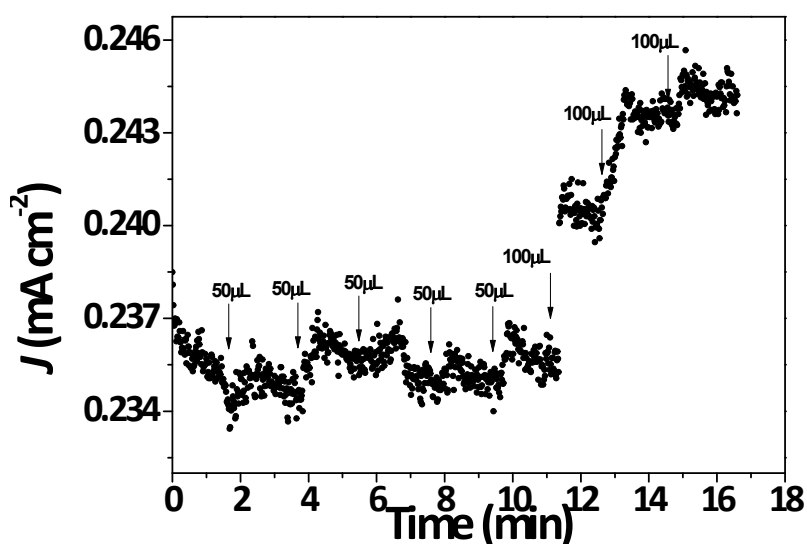
**Figure S6.** Energy Dispersive X-ray curve obtained from selected area of TEM image (Inset) illustrating the chemical information of the TiNT-ZnONR powder. The powder was obtained removing the formed film over the conductor glass substrate.

Figure S7, exhibit the chronoamperometry experiments using  $\text{TiINT} \rightarrow \text{ZnONR}$ ,  $\text{TiINT} + \text{gly} \rightarrow \text{ZnONR}$  and  $\text{TiINT} \rightarrow \text{ZnONr} + \text{gly}$  as photoanodes, where the light, provided by a 300 W Xenon lamp, was turned on and off at each 20 seconds. The results show that the electrodes only catalysis the water splitting under irradiation.



**Figure S7.** Chronoamperometry using  $\text{TiINT} \rightarrow \text{ZnONR}$ ,  $\text{TiINT} + \text{gly} \rightarrow \text{ZnONR}$  and  $\text{TiINT} \rightarrow \text{ZnONr} + \text{gly}$  as photoanodes, switch on and off the light at defined intervals of time.

In order to verify whether the photocurrent increases is not due to gly oxidation or detachment, the chronoamperometric experiment was performed using the pure ZnO electrode, adding gly during the experiment, Figure S8. Adding 50  $\mu\text{L}$  of gly  $0.01 \text{ mol L}^{-1}$  the photocurrent raised slightly, but soon falling, only if added 100  $\mu\text{L}$  of gly the photocurrent increase significantly. Considering that it was necessary a much higher amount of gly than used to prepare the films to increase the photocurrent, it's possible to dismiss the possibility of increased photocurrent due to gly detachment or oxidation. A similar experiment using ZnONR+gly was not performed since the gly must be consumed during the ZnONR growth process, as result, it is not freely available for participating in Redox process during the photoelectrocatalytic experiments.



**FigureS8.** Chronoamperometry of ZnO with glycine dosage in electrolyte solution under simulated sunlight at 1.23 V versus RHE.



Diffuse reflectance UV-Vis spectra of ZnONR, TiNT→ZnONR and TiNT+gly→ZnONR films, Figure S9, show absorption bands on UV region of spectrum. The intensity of these absorption bands are higher for the TiNT decorated films, due the contribution of TiNT which also absorbs UV light.

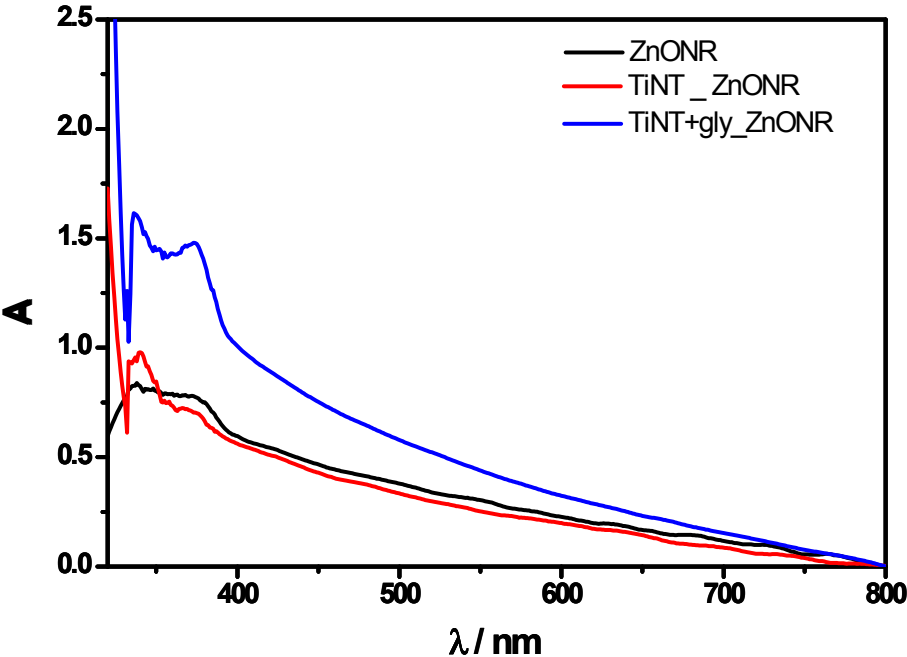


Figure S9. Diffuse reflectance UV-Vis spectra of ZnONR, TiNT→ZnONR and TiNT+gly→ZnONR films.

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