Supporting Information

TiO_2 nanotubes for solar water splitting: Vacuum annealing and Zr doping enhance water oxidation kinetics

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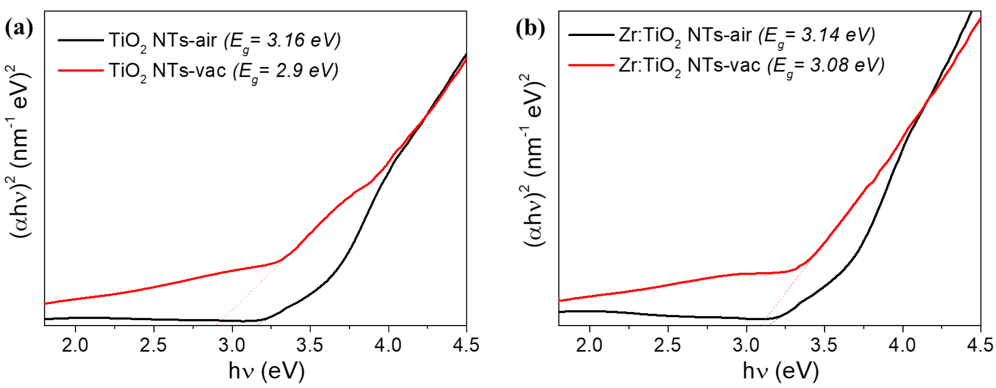
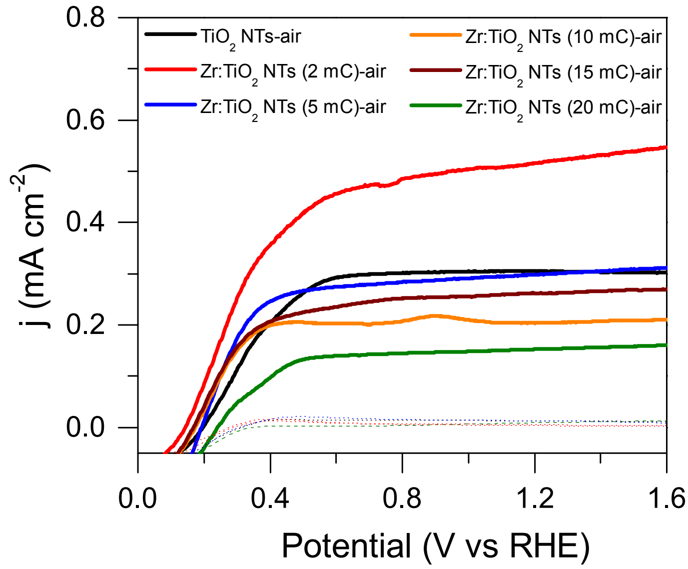


Figure S1. Tauc plots for direct optical transitions (a) TiO_2 and (b) Zr:TiO_2 NTs heat treated in different atmospheres. The derived bandgaps are showed in the corresponding plots.

(a)



(b)

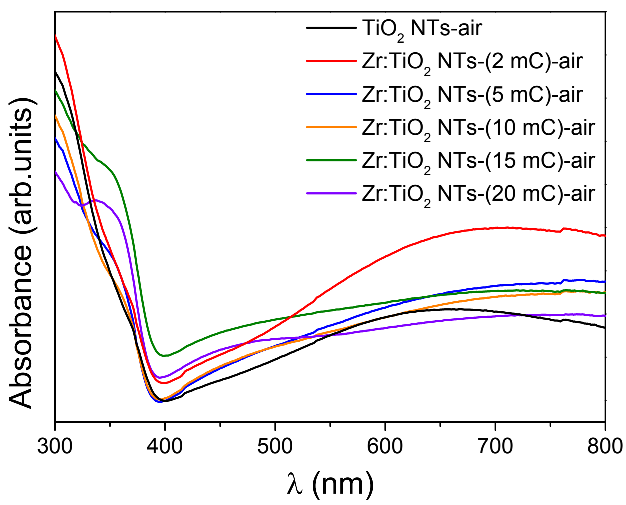
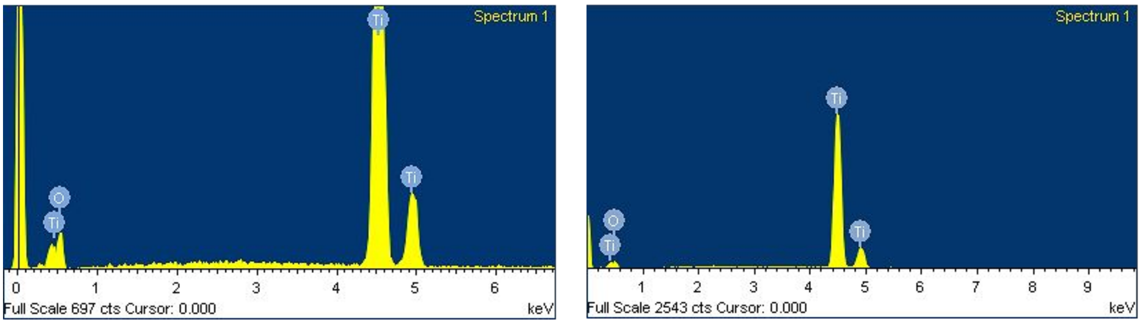


Figure S2.- **(a)** Photocurrents for water oxidation and **(b)** Absorbance spectra for undoped and Zr doped TiO_2 nanotubes with different dopant additions under air atmosphere.

Table S1. Photocurrent obtained through integration of the IPCE spectra with the Solar Spectrum for the calculation of the integrated current.

Atmosphere	TiO_2 NTs	Zr:TiO_2 NTs
Air	0.30 mA/cm^2	0.53 mA/cm^2
Vacuum	0.44 mA/cm^2	0.73 mA/cm^2



(a) **(b)**

Figure S3.- EDS analyses of the **(a)** TiO_2 and **(b)** Zr:TiO_2 NTs.

Supplementary Data Table S2.- EDS analysis of the TiO_2 and Zr:TiO_2 NTs.

	TiO_2	Zr:TiO_2
Ti (at. %)	33.33	33.33
O (at. %)	66.67	66.67

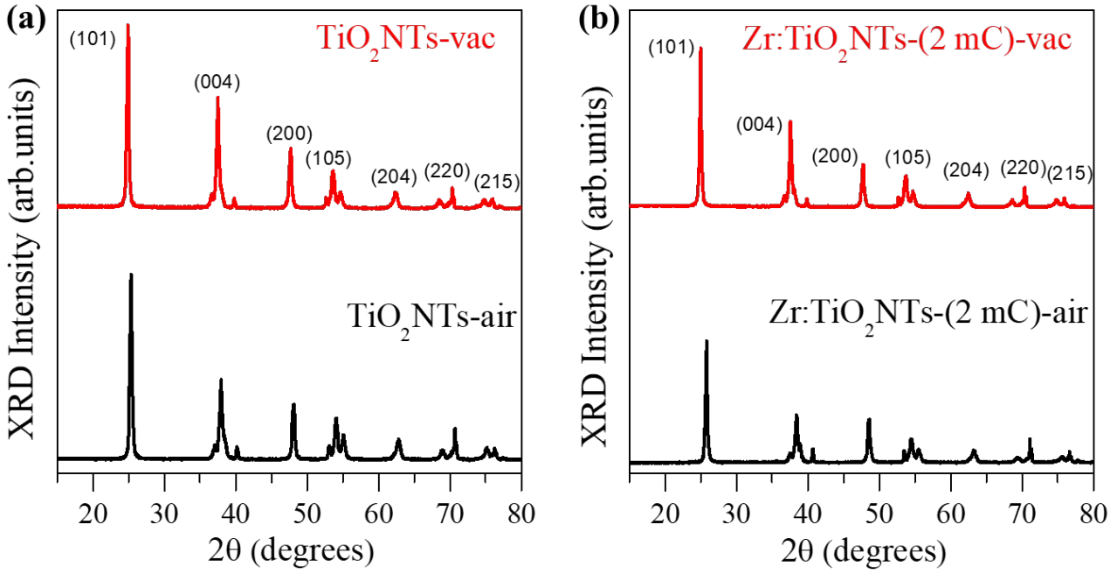


Figure S4.- X-rays diffractograms of TiO_2 nanotubes heat treated at both air and vacuum atmospheres **(a)** bare TiO_2 **(b)** Zr:TiO_2 NTs

Table S3. hkl parameters for TiO_2 samples with and with Zr addition under different thermal treatments. In all cases, the hkl parameters correspond to pure anatase.

hkl	**TiO_2 air (Å)**	**TiO_2 vacuum (Å)**	**TiO_2 Zr(2 mC) vacuum (Å)**	**TiO_2 Zr(15 mC) air (Å)**
101	3.5281	3.5405	3.5137	3.4673
400	2.3907	2.3621	2.3850	2.3753
200	1.9188	1.9212	1.8950	1.9395
105	1.6821	1.6851	1.6775	1.6907

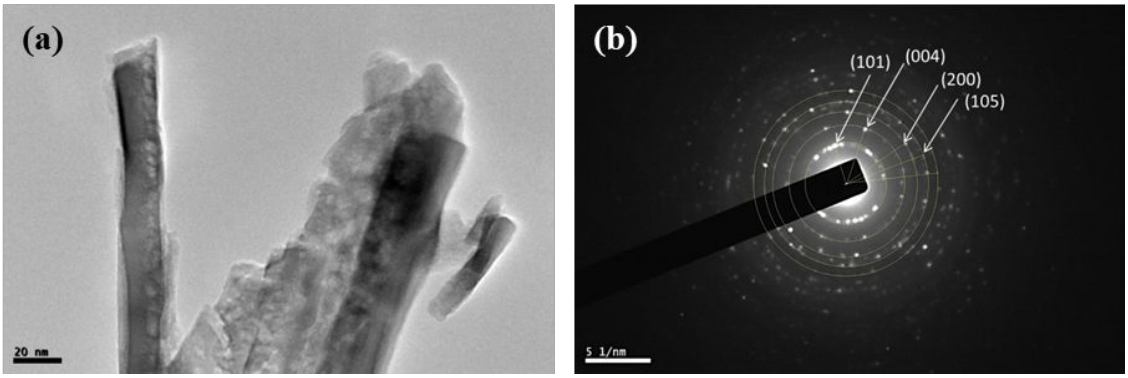


Figure S5.- **(a)** Representative TEM image of TiO_2 nanotubes and **(b)** SAED pattern of a TiO_2 15 mC Zr sample.

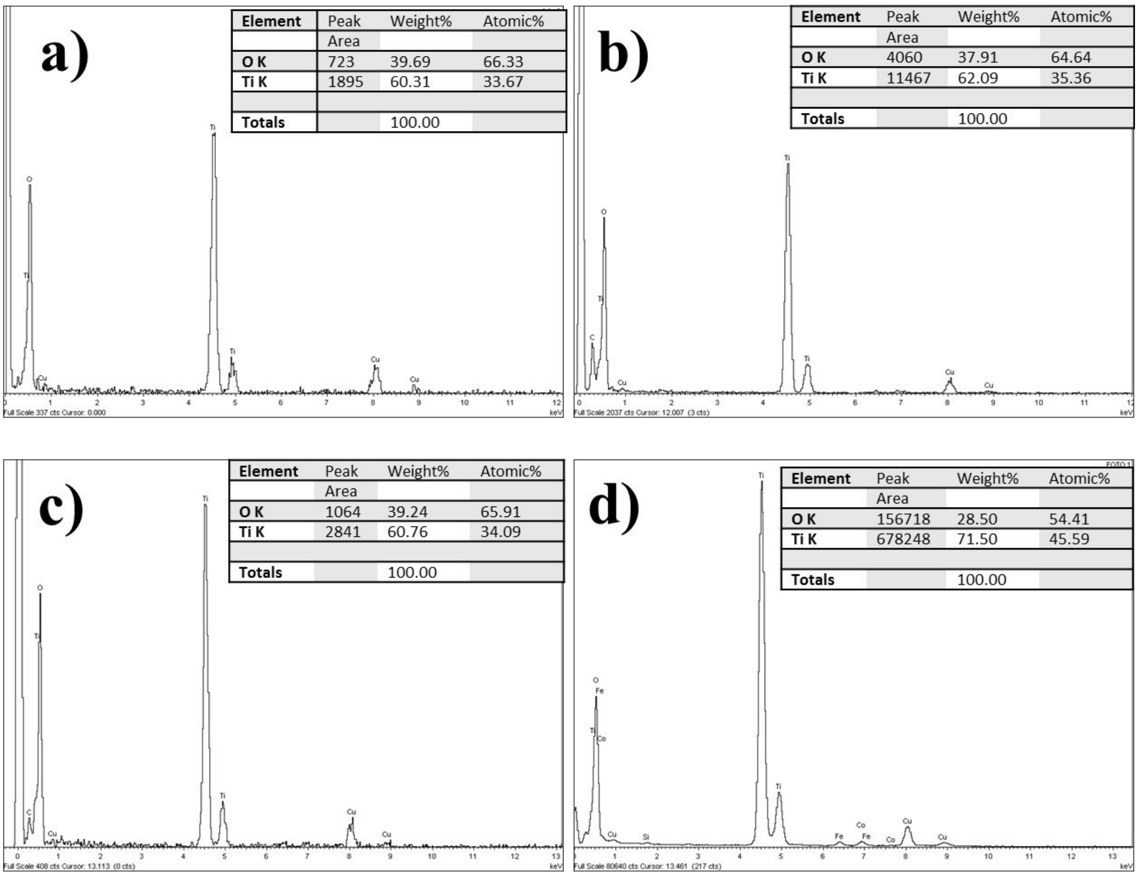


Figure S6. EDS analyses carried out by TEM on the samples **(a)** TiO_2 as prepared, **(b)** TiO_2 vacuum annealed, **(c)** TiO_2 2 mC Zr vacuum annealed and **(d)** TiO_2 15 mC Zr vacuum annealed.

Table S4. - XPS quantification carried out in the Zr:TiO_2 NTs samples under air and vacuum atmospheres.

Element	Air (% at.)	Vacuum (% at.)
O 1s	43.1	41.7
Ti 2p	12.0	13.1
Zr 3d	0.3	0.3

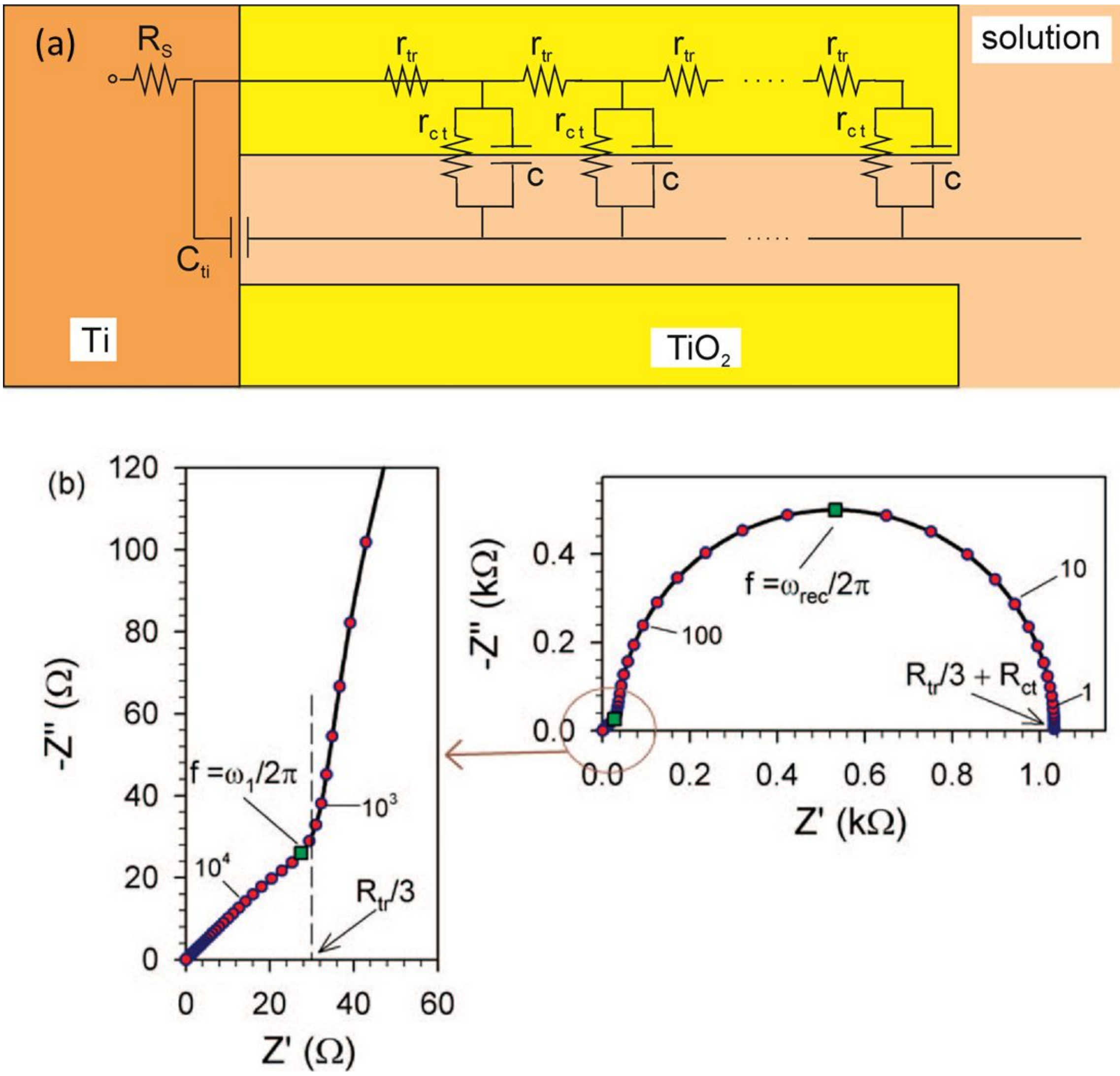


Figure S7.- (a) Equivalent circuit employed to fit the experimental impedance spectroscopy data. (b) Characteristic Nyquist plot of the nanotubes, with amplification of the high frequency region to show the 45 degree line related to transport resistance.

Table S5: Parameters extracted from the Mott-Schottky analysis showed in **Figure 5** of the main text.

		TiO_2 NTs air	**TiO_2 NTs vacuum**	**Zr:TiO_2 NTs air**	**Zr:TiO_2 NTs vacuum**
Dark	**V_{FB} (V vs RHE)**	0.11	0.2	0.12	0.16
Dark	**N_D (x10^{21} cm^{-3})**	1.9	1.9	2.1	1.3
Light	**V_{FB} (V vs RHE)**	0.14	0.18	0.12	0.16
Light	**N_D (x10^{21} cm^{-3})**	2.1	1.3	2.5	2.2

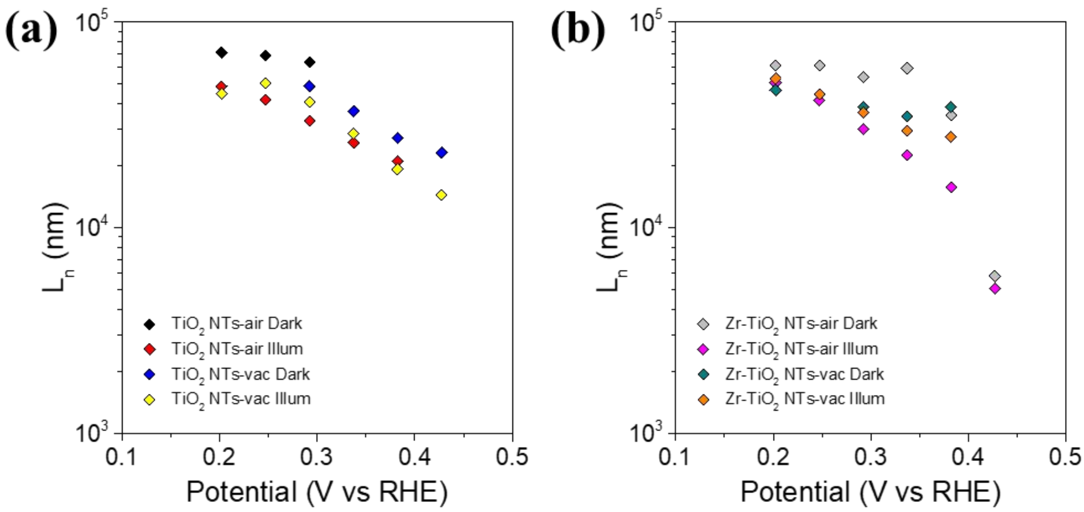


Figure S8.- Carrier diffusion length calculated for **(a)** undoped and **(b)** Zr doped TiO_2 nanotubes for samples thermally treated in air and vacuum.

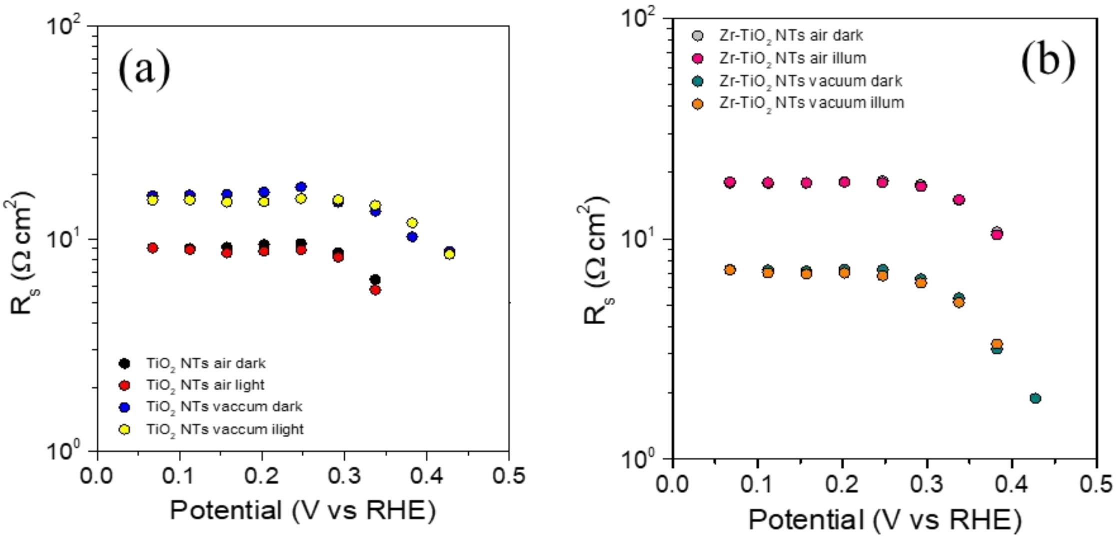


Figure S9.- Series resistance (R_s) for TiO_2 nanotubes thermally treated in air and vacuum **(a)** bare **(b)** Zr-doped.

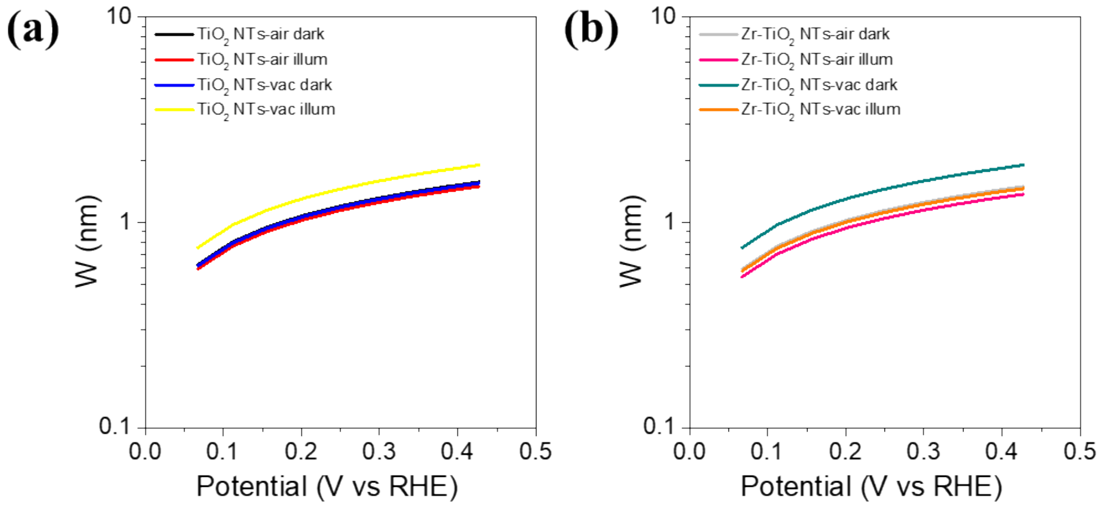


Figure S10.- Calculation of the space charge zone (w) for TiO_2 nanotubes **(a)** bare and **(b)** Zr-doped, thermally treated in air and in vacuum.