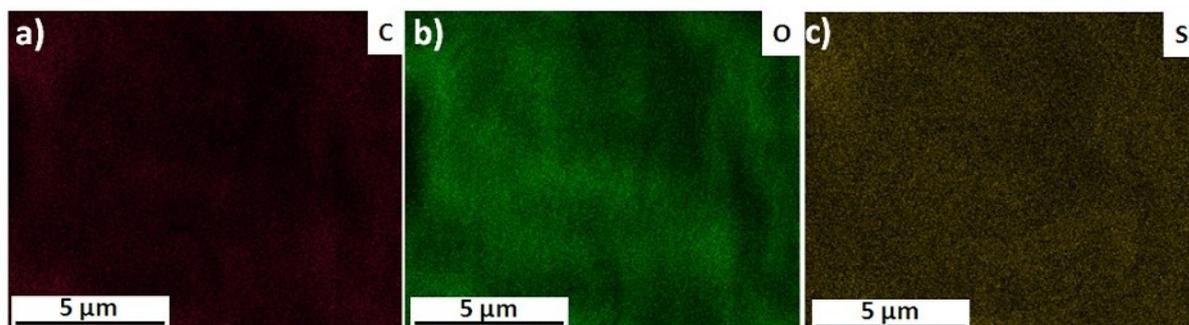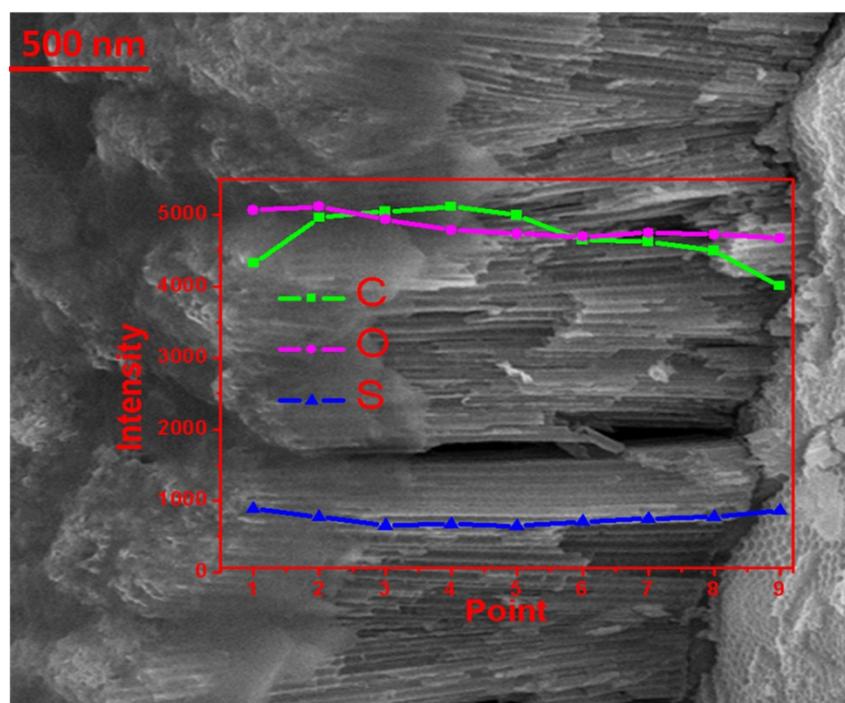# Electronic supplementary information

Highly stable organic-inorganic junction composed of hydrogenated titania nanotubes infiltrated by conducting polymer

EDX analysis performed at the surface and across the titania layer

Fig. S1 Distribution of (a) carbon, (b) oxygen and (c) sulphur over the H-TiO$_2$NTs/pEDOT:PSS composite layer.
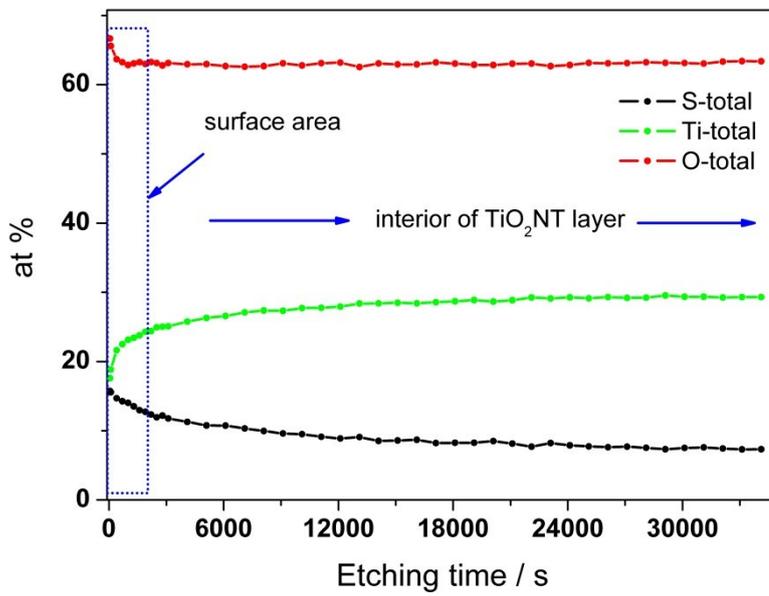

Fig. S2 The distribution of carbon, oxygen and sulphur across the composite H-TiO$_2$NTs/pEDOT:PSS material.

Photography of samples

Fig. S3 Photography of a) H-TiO$_2$NTs and b) H-TiO$_2$NTs/pEDOT:PSS sample.

XPS analysis

Fig. S4 A distribution of sulphur, carbon and oxygen across the H-TiO$_2$NTs/pEDOT:PSS samples inspected under the XPS etching mode.

Electrochemical Impedance spectroscopy

The interpretation of EEQC elements

The electrolyte resistance was assigned as R_e, whereas the subsequent EEQC parts were attributed to the compact oxide film (CPE_1R_1) and highly ordered nanotubes ($CPE_2R_2W_o$). As it was reported by Brug[1], a constant phase element was used because of electrode inhomogeneity. The impedance of CPE is defined as $Z = Q^{-1}(i\omega)^{-\alpha}$, where energy dispersion denoted as α is considered. Its value was in the range between 0.85 and 0.99. In the EEQC part attributed to processes occurring in the tubular film, the Warburg open element is present. The W_o is assigned to the finite length diffusion with reflective boundary and described by:

$$Z_{W_0}(\omega) = \frac{\omega_{or}}{\sqrt{\omega}}(1-j)\coth[W_{OC}\sqrt{j\omega}] \quad (3)$$

where W_{or} stays for Warburg coefficient, $W_{oc} = d/D^{0.5}$. In the case of the studied material, W_o is related to the charge transport within tubular titania down to the blocking metal oxide support. The calculated values for each element in EEQC for a pristine and hydrogenated sample are collected in Table S1. As it could be seen, in the case of pure TiO_2, the huge difference between R_1 and R_2 is present due to high conductivity of the walls when compared to the base semiconductor film.[2] Thus, the observed response is mainly attributed to the bottom oxide, while the TiO_2 nanotubular layer has an impact on the shift of the Fermi level of the material and surface chemistry effects.
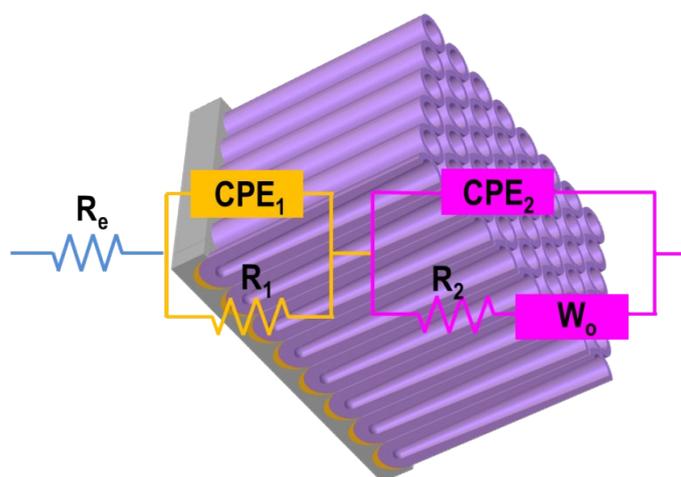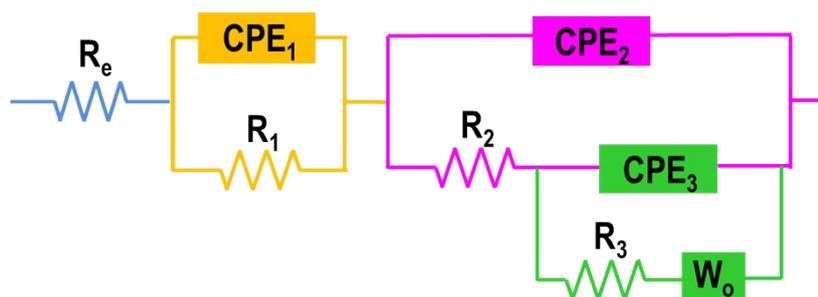

Fig. S5 The scheme of an electric equivalent circuit used for impedance spectra fitting for pure and hydrogenated titania samples.

Table S1. The calculated values for electric equivalent circuit elements for pure and hydrogenated TiO$_2$ titania nanotubes.

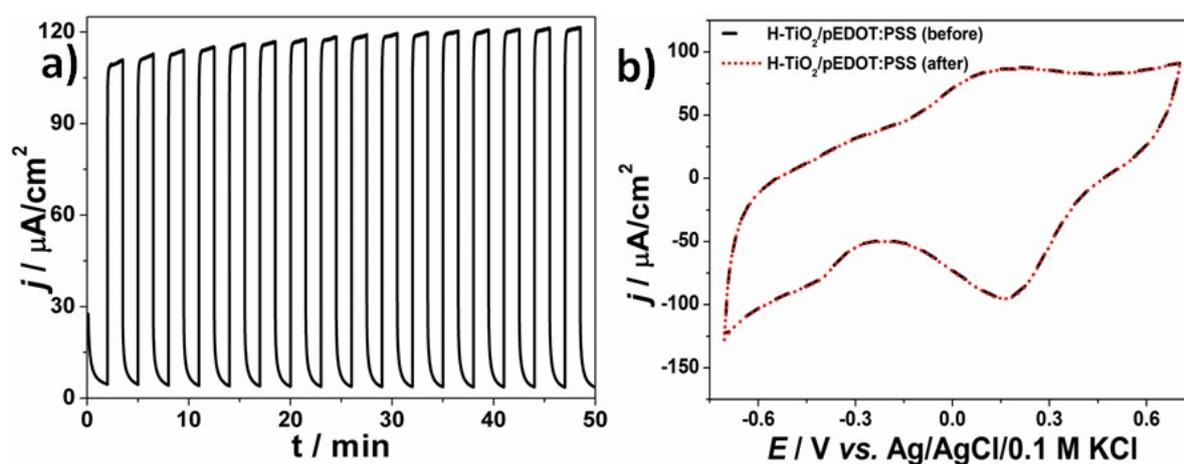| material	Re / Ω	R$_1$/ Ω	CPE$_1$ / Ω^{-1}s^n	R$_2$ / Ω	CPE$_2$/ Ω^{-1}s^n	W$_{or}$ / Ω s$^{-0.5}$	W$_{oc}$
TiO$_2$	5.2	7756	1×10^{-5}	7.14	7.5×10^{-6}	5.24	1.98×10^{-5}
H-TiO$_2$	8.1	0.64	8.37×10^{-5}	4.46	1.8×10^{-4}	9.2×10^{-6}	8.78×10^{-10}
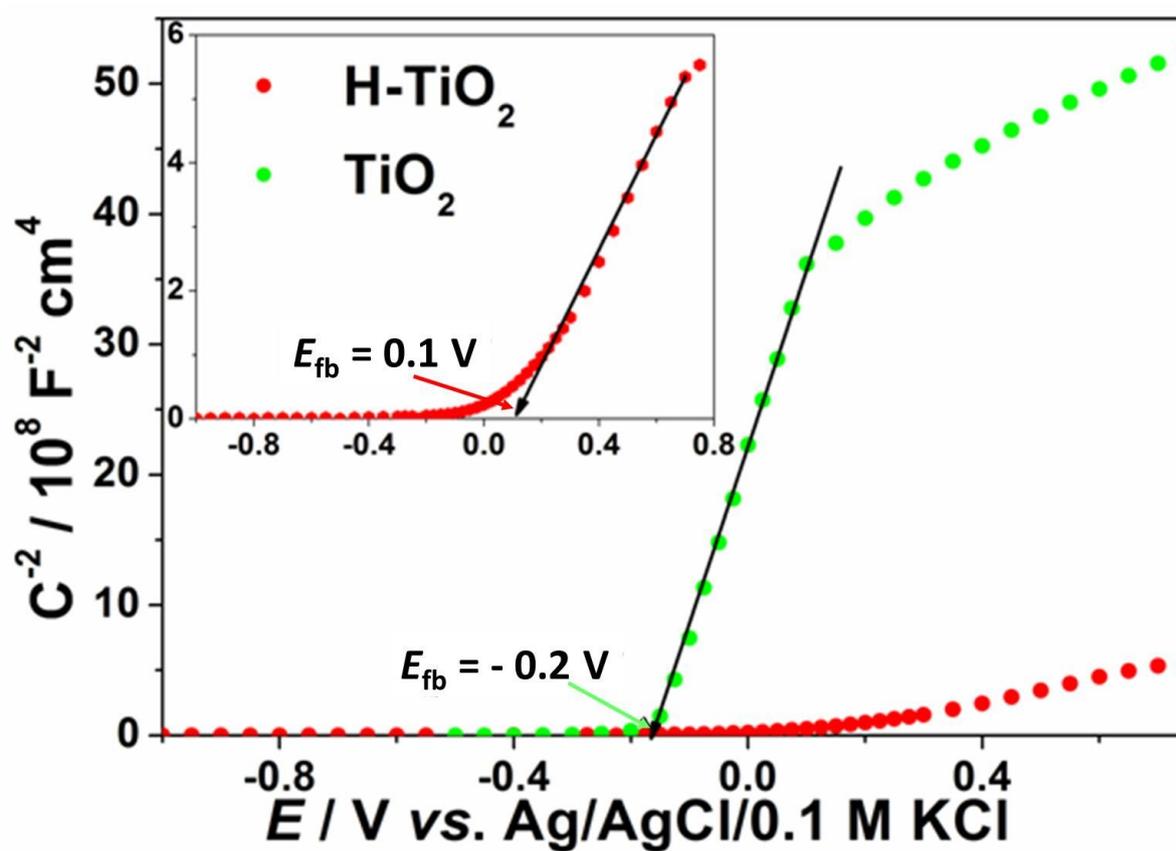
Fig. S6 The Mott-Schottky plot for pristine and hydrogenated TiO$_2$NTs.

Fig. S7 The scheme of the electric equivalent circuit used for impedance spectra fitting for composite H-TiO$_2$NTs/pEDOT:PSS material.

Table S2 The calculated values for electric equivalent circuit elements for H-TiO$_2$NTs/pEDOT:PSS (s = 0.5 cm^2).

element	value	element	value
Re / Ω	7.2	CPE$_3$ / Ω^{-1}s^n	2×10^{-5}
CPE$_1$ / Ω^{-1}s^n	5.05×10^{-4}	R$_3$ / Ω	197.29
R$_1$ / Ω	10.12	Wor / Ω s$^{-0.5}$	9.33×10^{-4}
CPE$_2$ / Ω^{-1}s^n	1.73×10^{-4}	Woc / s$^{-0.5}$	2.77×10^{-7}
R$_2$ / Ω	742.96		

Fig. S8 a) Transient photocurrent registered for H-TiO$_2$NTs/pEDOT:PSS under prolonged irradiation, b) cyclic voltammetry curve of composite electrode obtained before and after photocurrent measurements.

References:

1 G. J. Brug, A. L. G. Van Den Eeden, M. Sluyters-Rehbach and J. H. Sluyters, *J Electroanal. Chem.*, 1984, **175**, 275.

2 H. Wu, D. Li, X. Zhu, C. Yang, D. Liu, X. Chen, Y. Song and L. Lu, *Electrochim. Acta*, 2014, **116**, 129.