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# Electronic Supplementary Information

*Titania nanotubes infiltrated with conducting polymer PEDOT modified by Prussian Blue– a novel type of organic-inorganic heterojunction characterised with enhanced photoactivity*

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## Experimental details

### a) $TiO_2$ formation

Highly ordered $TiO_2$NTs samples were prepared via two-step anodization according to the previously optimized procedure. Before anodization, the substrate sample (Ti plate, Steam, 99.7%) was ultrasonically cleaned in the following order: in acetone, ethanol and water for 10 minutes in each solvent, and ultimately dried in the air. The process was realized in a two-electrode configuration at room temperature, where the titanium plate served as an anode and the platinum mesh as a cathode with a fixed distance of 2 cm between them. The first anodization took place in the electrolyte containing: ethylene glycol (EG), 0.27 M $NH_4F$ and 1 vol. % of deionized water. Anodization was performed at 40 V for 2 h, with the initial voltage rate of 0.1 V/s. Then, the titanium plate was immersed for 12 h in 0.5% wt. solution of oxalic acid in order to first remove the rugged nanotube layer. The second anodization process was performed on the as-cleaned titanium plate under the same conditions as those during the first anodization. In order to remove surface debris, the titanium plates covered with nanotubes were immersed in 0.05% wt. HF for 180 s. After second anodization, the samples were rinsed with deionised water, dried in air and thermally treated at 450°C for 2 h with a heating rate of 2°C/min to transform the amorphous $TiO_2$ into a crystalline phase.

Finally, $TiO_2$NTs were subjected to the hydrogen environment in a plasma reactor (Electronic Diener) operating at power of 40 W, at room temperature, for 60 min. Electrochemical and photoelectrochemical properties of titania NT after hydrogenation process were described in our previous report.[1]

### b) Deposition of pEDOT/Fehcf

Electrochemical polymerization was carried out to prepare $TiO_2$NTs/PEDOT:Fehcf. Electrochemical deposition was performed according to the two step procedure proposed previously[2, 3] The first step covers potentiostatic electropolymerisation from an aqueous solution containing monomer EDOT and $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. As a working electrode flat titanium plate or hydrogenated titania NTs layer was used. The reference electrode was Ag/AgCl/0.1 M KCl whereas a platinum mesh was used as a counter electrode. The process was performed at the potential of 1.6 V *vs*. Ag/AgCl/0.1 M KCl consuming the charge of 30 mC $cm^{-2}$. During this stage pEDOT with hexacyanoferrates counter-ions $Fe(CN)_6^{3-/4-}$ is obtained. The formation of Fehcf inside polymer matrix is based on a potentiodynamic polarisation of pEDOT/FeCN in aqueous $FeCl_3$ solution (the source of $Fe^{III}$ ions) in the potential range from -0.4 to + 0.9 V *vs*. Ag/AgCl/0.1M KCl. The final potential applied to the film was +0.56 V *vs*. Ag/AgCl/0.1M KCl.

The reaction of inorganic redox network Fehcf formation could be presented as follows:

$$yFe(CN)_6^{3-/4-} + xFe^{III/II} \rightarrow Fe_x^{III/II}[Fe^{III/II}(CN)_6]_y$$

Finally, the working electrode was washed with deionized water and immersed in 0.5 M $K_2SO_4$ for further electrochemical characterisation.

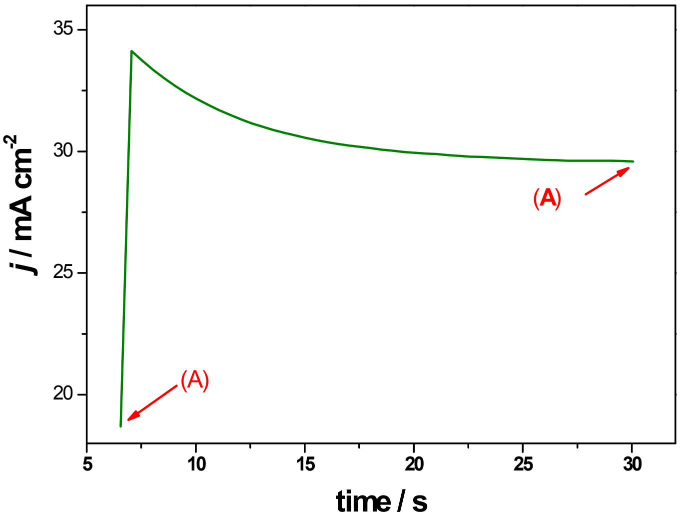

**Figure S1.** Potentiostatic deposition of pEDOT:FehCN onto $TiO_2$ NT

(deposition conditions: $E$ = +1.6 V *vs*. Ag/AgCl/0.1 M KCl, $Q$ = 30 mC $cm^{-2}$).

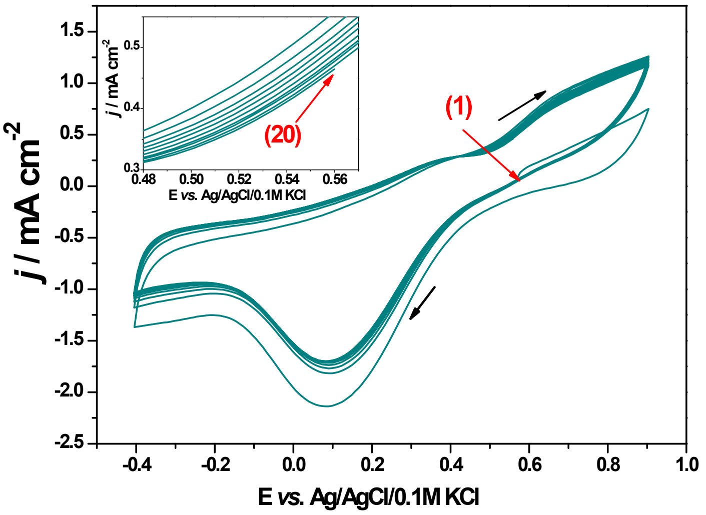

**Figure S2**. Potentiodynamic polarisation of $TiO_2$NT/pEDOT:Fehcf in $FeCl_3$ solution ($v$ = 20 mV $s^{-1}$).

### c) Characterisation of morphology, structural and optical properties

The surface morphology and cross-section were examined using the Schottky field emission scanning electron microscopy (FEI Quanta FEG 250) with an ET secondary electron detector. The beam accelerating voltage was kept at 10 kV. For elemental analysis, the Energy Dispersive X-ray Spectroscopy (EDX) was performed by EDAX Genesis APEX 2i with ApolloX SDD spectrometer in a particular area of each sample. In order to confirm uniform polymer deposition, the elemental analysis was completed on the surface and across the composite layer.

The chemical nature of elements and binding properties of the surface was studied using the X-ray photoelectron spectroscopy (XPS), by means of the Escalab 250Xi from ThermoFisher Scientific. High-resolution spectra were recorded at the energy step size of 0.1 eV at a pass energy of 10 eV. In order to normalize the spectroscopic measurements, the X axis (binding energy, $E_{bin}$) from XPS spectrum was calibrated for peak characteristics of neutral carbon 1s ($E_{bin}$ = 284.6 eV).

The UV-Vis reflectance spectra of titania nanotubes were measured with a dual beam UV-Vis spectrophotometer (Lambda 35, Perkin-Elmer) equipped with a diffuse reflectance accessory. The spectra were registered in the range of 300 - 700 nm, with a scanning speed of 60 nm/min.

The Raman spectra were recorded by a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation, by means of an argon ion laser emitting at 514 nm operating at 5% of its total power (50 mW).

### d) Electrochemical and photoelectrochemical measurements

Electrochemical measurements were carried out using an AutoLab PGStat 302N potentionstat-galvanostat system (Methrom, Autolab) in the standard three-electrode assembly.

Concerning electrodes arrangement, the following set up was used:
- working electrode: titanium plate covered with hydrogenated titania nanotubes or H-$TiO_2$/pEDOT:Fehcf ($Q$ = 30 mC $cm^{-2}$) characterised with surface area of 0.3 $cm^2$).
- counter electrode: Platinum mesh,
- reference electrode: Ag/AgCl/0.1M KCl.

All potentials given in the main manuscript body were given versus Ag/AgCl/0.1M KCl.
Electrodes were tested in contact with deaerated aqueous 0.5 M $K_2SO_4$ electrolyte. An electrochemical cell was equipped with a quartz window. The photoactive layers were illuminated with a 150 W Xenon lamp (Osram XBO 150) and an AM 1.5 filter was used to obtain simulated solar light and the automated light chopper with a period of 90 s was used as a light source. The light source was placed in the front of the photoelectrode and the light falls perpendicularly to the Ti plate covered by $TiO_2NT$ or $TiO_2NT$/pEDOT:Fehcf. The irradiance of incident light was measured to be 100 $mW/cm^2$ using a reference cell (Si solar cell, Rera). The photocurrent measurements were carried out at + 0.8 V *vs.* Ag/AgCl/0.1M KCl bias voltage.

# Results

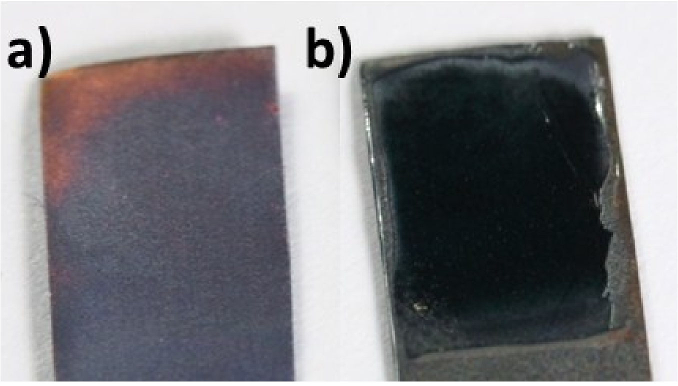

**Figure S3.** Photography of a) $TiO_2$ and b) $TiO_2$/pEDOT:Fehcf.

**XPS spectra**

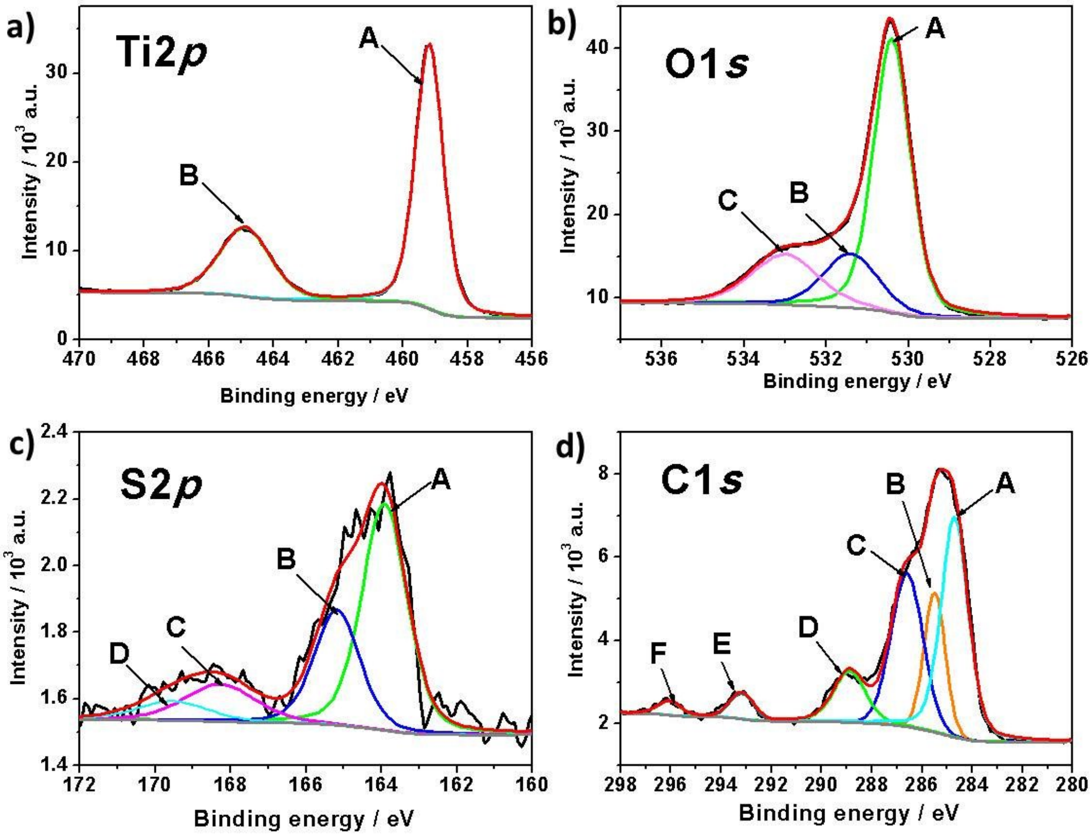

**Figure S4.** XPS spectra of a) Ti2*p*, b) O1*s*, c) S2*p* and d) C1*s* registered for $TiO_2$/pEDOT:Fehcf sample ($Q$ = 30 mC $cm^{-2}$). The interpretation of each fitted signal marked by A-F letters was given in the main manuscript body.

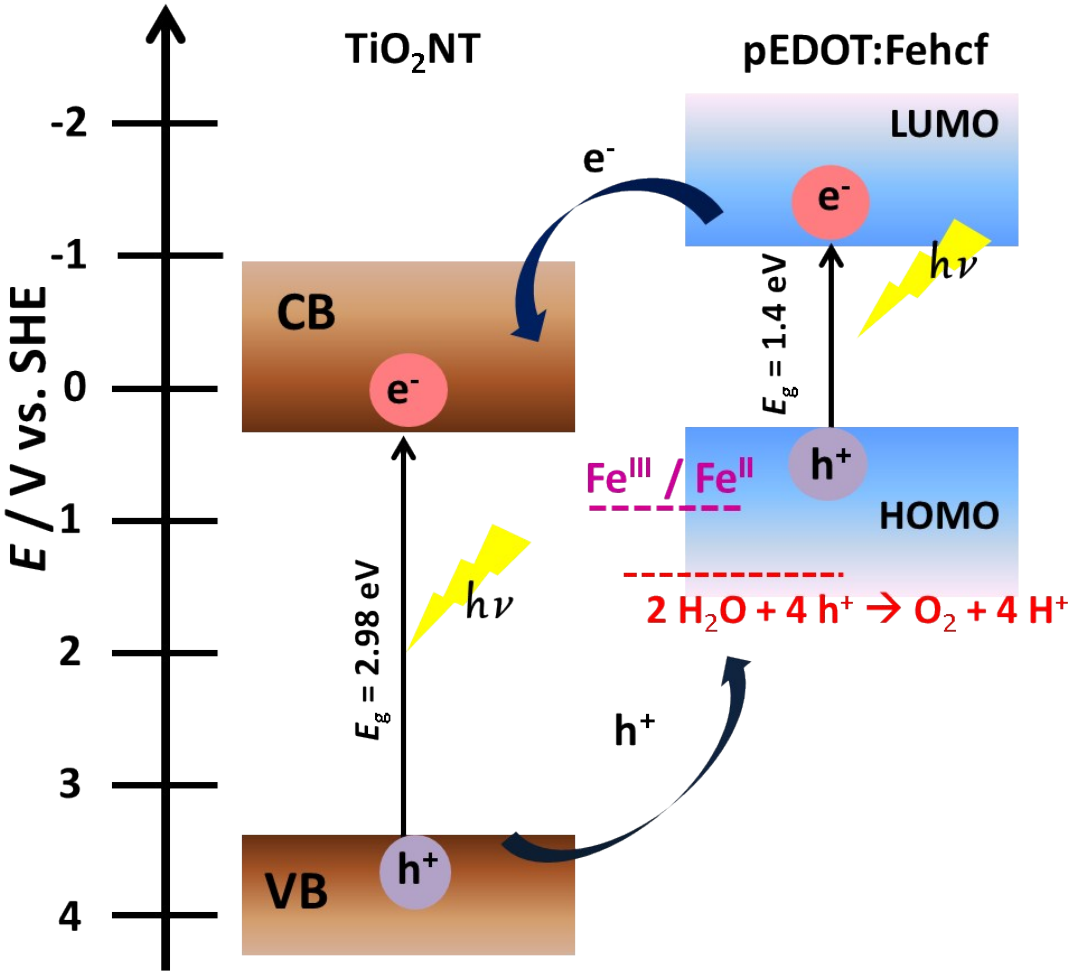

**Figure S5.** Scheme showing the band energy levels and the synergistic effect of pEDOT:Fehcf and $TiO_2$NT for photocurrent generation ($Fe^{III}/Fe^{II}$ represents low spin iron centre of PB). [1,4,5]

## References

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