

Electronic Supplementary Information

Interfacial Charge Transfer in Functionalized Multi-walled Carbon

Nanotube@TiO₂ nanofibres

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Nanocarbon-TiO₂ interface approximation

First indications in favor of large interfaces come from the TEM analyses of the hybrids pointing to the lack of CNT aggregation or segregation on the surface.¹ This implies that ox-MWNTs are uniformly dispersed within the metal oxide mesoporous structure. Considering these assumptions, the total interface (I) is given by the specific surface area of CNTs (SSA) and the fraction of surface coverage (f). Taking a value of $f = 0.5$ as an estimate from HRTEM imaging and with $SSA = 223\text{m}^2/\text{g}$ from the supplier of MWNTs, the interface is $11\text{m}^2/\text{g}$. For comparison, this is 25% of the TiO₂-air interface and 10% of the interface between TiO₂ nanocrystals.

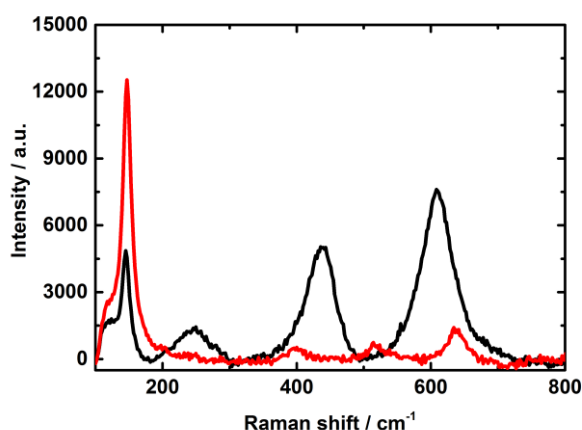


Figure S1 Raman spectra of electrospun TiO₂ fibres with anatase (red spectrum) characteristics. After several accumulations as well as using high laser power, rutile (black spectrum) was obtained which means that these conditions produce photoinduced phase transformation. This circumstance must be taken into account in all further spectroscopic studies.

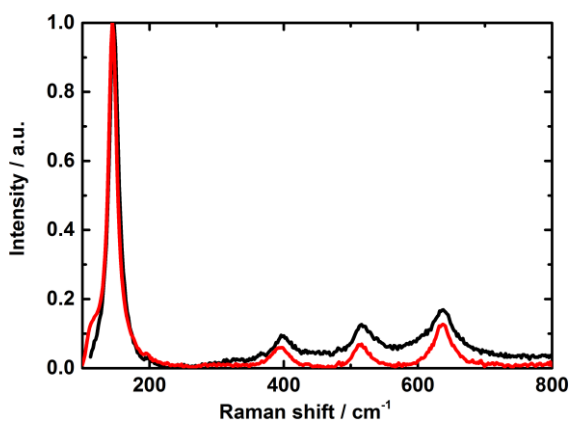


Figure S2. Raman spectra of TiO₂ fibres before (black spectra) and after (red spectra) femtosecond transient spectroscopy. Laser is neither damaging the sample nor inducing phase transformation.

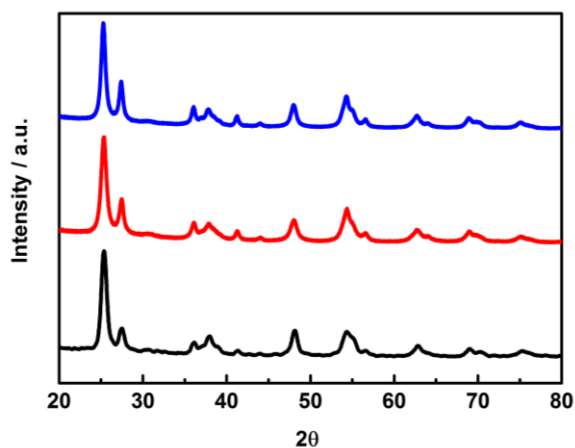


Figure S3. X-ray diffraction patterns of TiO₂ fibres (black line) and oxMWCNTs@TiO₂ hybrid fibres for 1vol.% (red line) and 5vol.% (blue line) of oxMWCNTs. They corresponds to a mixture of anatase and rutile phases with similar phase ratio for all the samples.

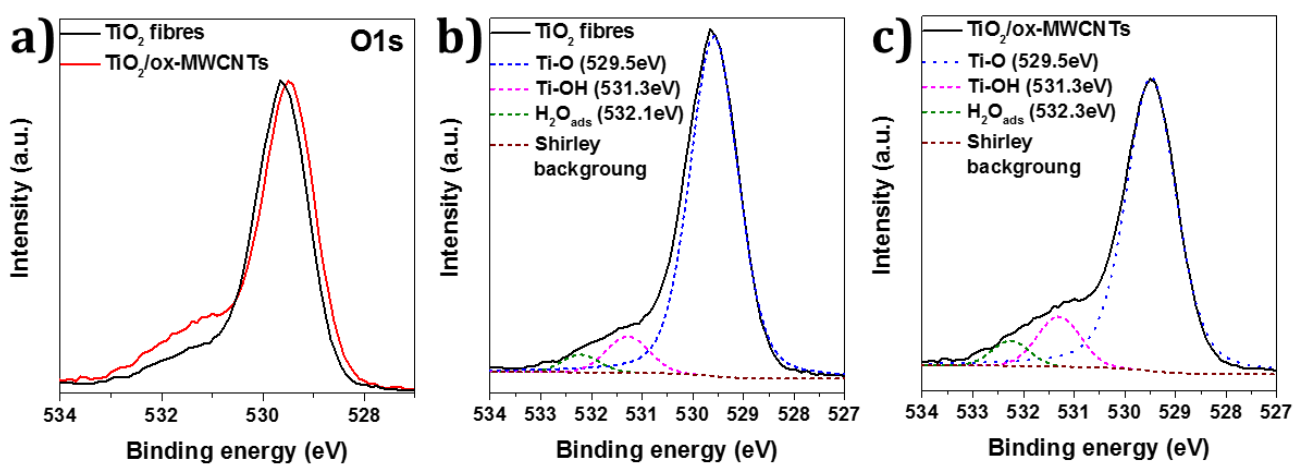


Figure S4. a) XPS spectra of O1s region of TiO₂ and oxMWCNT@TiO₂ hybrid and deconvolution of b) TiO₂ and c) oxMWCNT@TiO₂ spectra using mixed Gaussians/Lorentzian fittings. The hybrid shows higher signal intensity between 530.5-533 eV region than pure TiO₂ fibres which could be associated to different O environments. Thus, in the hybrid material, the possible Ti-O-C formed at the interface can contribute to the higher signal observed.

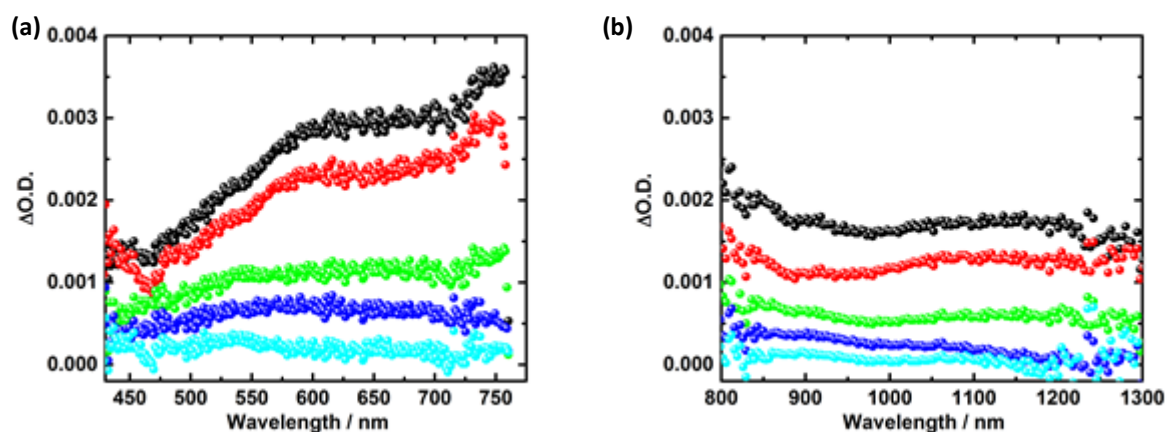


Figure S5. Femtosecond laser photolysis transient absorption spectra recorded upon 258 nm excitation (200 nJ/pulse) of solaronix TiO₂ film (a) vis, and (b) near-IR region deposited on quartz with time delays of 2 ps (black), 10 ps (red), 100 ps (green), 500 ps (blue), and 5000 ps (cyan) after the laser pulse. Visible and near-IR spectra were recorded at two different spots.

Table S1. Lifetimes and pre-exponential factors obtained after tri-exponential fittings of the time absorption spectra at 600 nm, and 1000 nm for TiO₂ fibres and oxMWCNT@TiO₂ hybrids

λ (nm)	a_1	τ_1 (ps)	a_2	τ_2 (ps)	a_3	τ_3 (ps)
TiO₂						
600 nm	-7.9×10^{-4}	5.9	-7.4×10^{-4}	55.1	-6.2×10^{-4}	366.7
1000 nm	2.5×10^{-3}	6.1	8.9×10^{-4}	35.8	2.7×10^{-4}	342.5
1vol%oxMWCNT@TiO₂						
500 nm	-3.4×10^{-3}	3.8	-3.0×10^{-3}	23.1	8.4×10^{-4}	1394.4
700 nm	2.6×10^{-3}	3.7	4.7×10^{-4}	38.1	-	-
1000 nm	1.2×10^{-3}	4.2	4.7×10^{-3}	42.8	9.9×10^{-4}	901.6
5vol%oxMWCNT@TiO₂						
500 nm	-1.8×10^{-3}	3.0	-1.5×10^{-3}	21.0	2.6×10^{-3}	4192.0
700 nm	6.3×10^{-3}	1.0	1.3×10^{-3}	10.2	6.5×10^{-4}	1479.9
1000 nm	6.8×10^{-3}	4.0	3.5×10^{-3}	27.2	7.6×10^{-4}	408.7

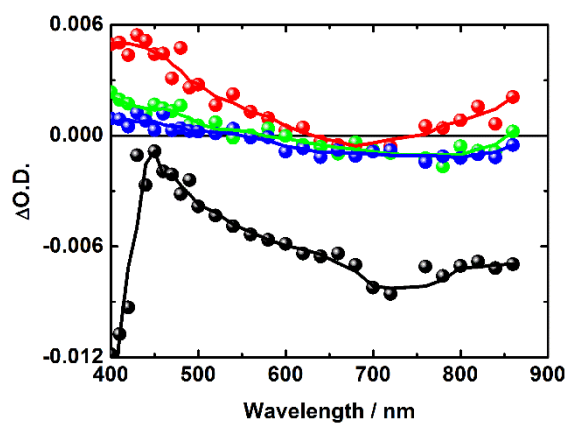


Figure S6. Nanosecond laser photolysis transient absorption spectra recorded upon 355 nm excitation (~ 8 mJ/pulse, 150 fs FWHM) of TiO_2 nanofibers dispersions in D_2O with time delays of 30 ns (black), 100 ns (red), 200 ns (blue), and 300 ns (green).

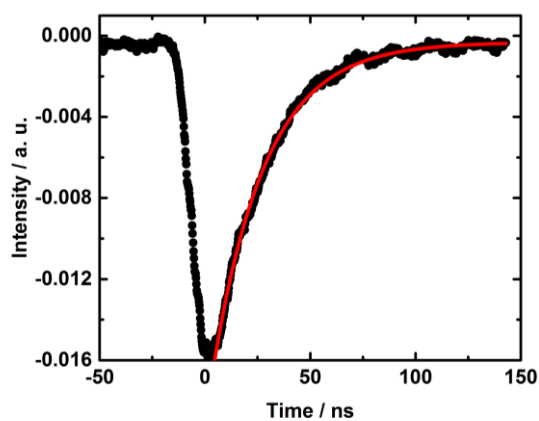


Figure S7. Emission time profile (black) and exponential decay fit (red) monitored upon 355 nm excitation (~ 8 mJ/pulse, 5 ns (FWHM)) of TiO_2 nanofibres monitored at 450 nm.

References

- 1) A. Moya, A. Cherevan, S. Marchesan, P. Gebhardt, M. Prato, D. Eder and J. J. Vilatela, *Appl. Catal. B Environ.*, **2015**, *179*, 574–582.