

## Electronic Supplementary Information

### Interfacial Charge Transfer in Functionalized Multi-walled Carbon

#### Nanotube@TiO<sub>2</sub> nanofibres

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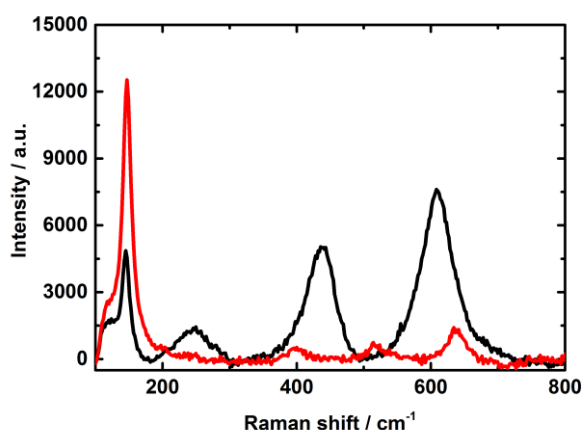
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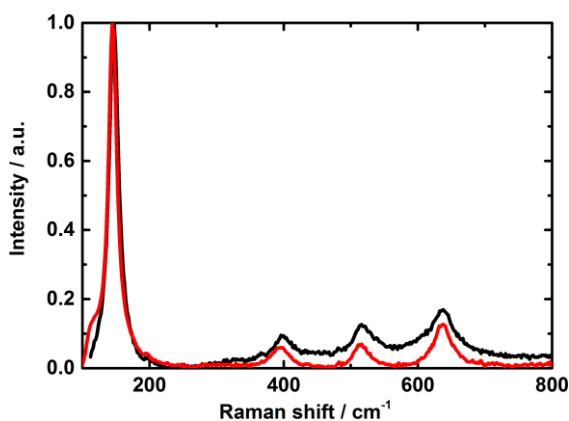
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## Nanocarbon-TiO<sub>2</sub> interface approximation

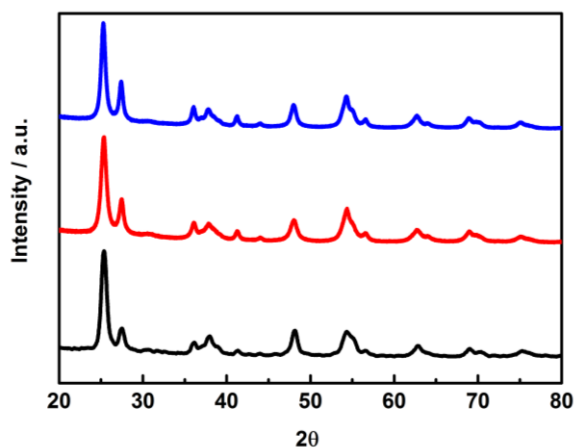
First indications in favor of large interfaces come from the TEM analyses of the hybrids pointing to the lack of CNT aggregation or segregation on the surface.<sup>1</sup> This implies that ox-MWNTs are uniformly dispersed within the metal oxide mesoporous structure. Considering these assumptions, the 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 TiO<sub>2</sub>-air interface and 10% of the interface between TiO<sub>2</sub> nanocrystals.



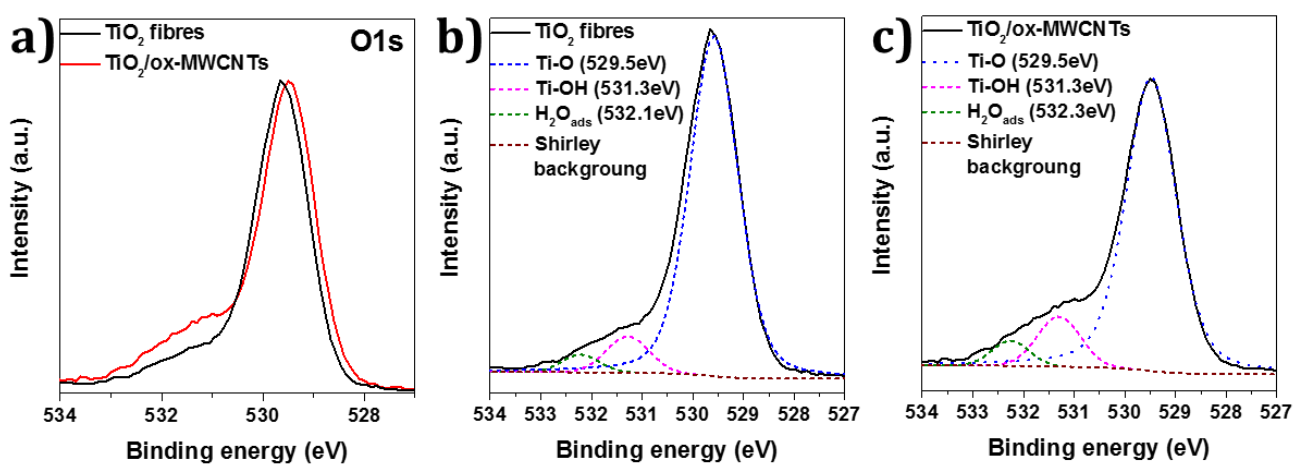
**Figure S1** Raman spectra of electrospun TiO<sub>2</sub> fibres with anatase (red spectrum) characteristics. After several accumulations as well as using high laser power, rutile (black spectrum) was obtained which means that these conditions produce photoinduced phase transformation. This circumstance must be taken into account in all further spectroscopic studies.



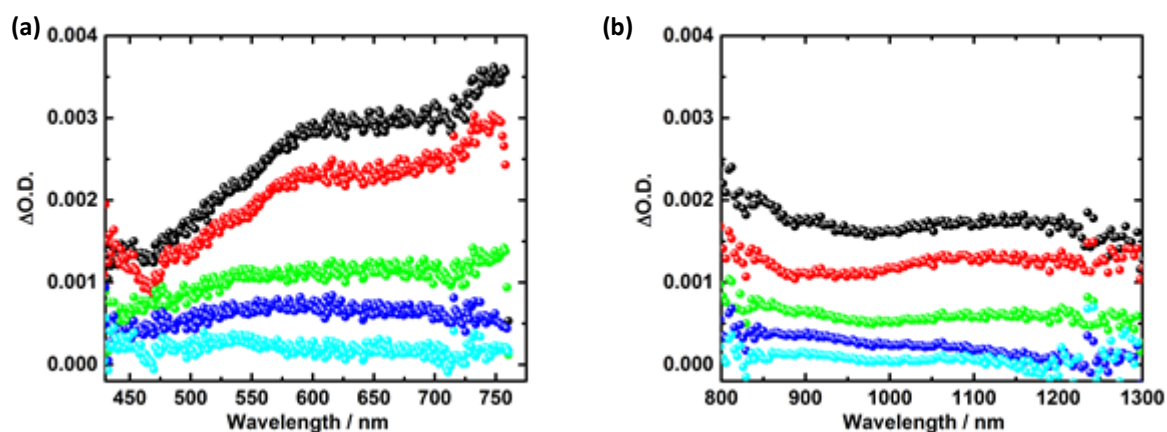
**Figure S2.** Raman spectra of TiO<sub>2</sub> fibres before (black spectra) and after (red spectra) femtosecond transient spectroscopy. Laser is neither damaging the sample nor inducing phase transformation.



**Figure S3.** X-ray diffraction patterns of TiO<sub>2</sub> fibres (black line) and oxMWCNTs@TiO<sub>2</sub> 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.



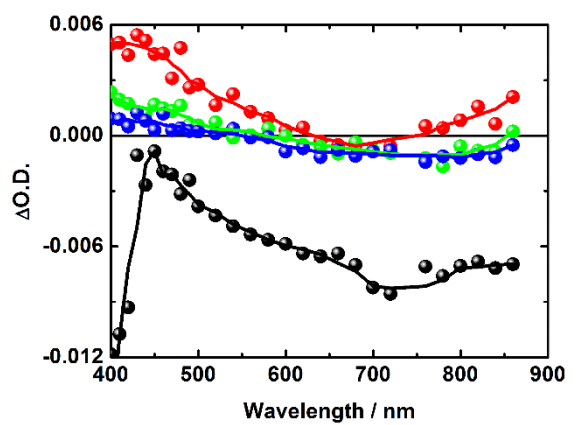
**Figure S4.** a) XPS spectra of O1s region of TiO<sub>2</sub> and oxMWCNT@TiO<sub>2</sub> hybrid and deconvolution of b) TiO<sub>2</sub> and c) oxMWCNT@TiO<sub>2</sub> spectra using mixed Gaussians/Lorentzian fittings. The hybrid shows higher signal intensity between 530.5-533 eV region than pure TiO<sub>2</sub> 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.



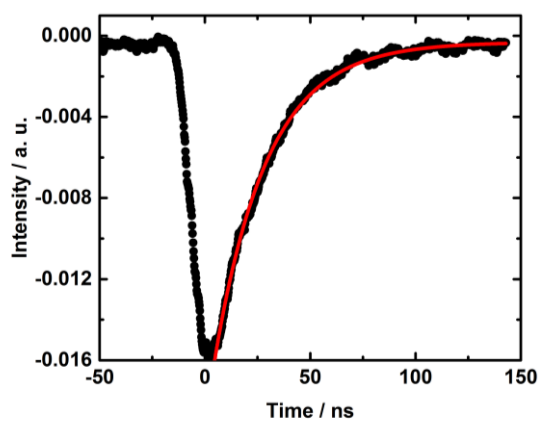
**Figure S5.** Femtosecond laser photolysis transient absorption spectra recorded upon 258 nm excitation (200 nJ/pulse) of solaronix TiO<sub>2</sub> film (a) vis, and (b) near-IR region deposited on quartz with time delays of 2 ps (black), 10 ps (red), 100 ps (green), 500 ps (blue), and 5000 ps (cyan) 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 TiO<sub>2</sub> fibres and oxMWCNT@TiO<sub>2</sub> hybrids

$\lambda$ (nm)	$a_1$	$\tau_1$ (ps)	$a_2$	$\tau_2$ (ps)	$a_3$	$\tau_3$ (ps)
<b>TiO<sub>2</sub></b>						
600 nm	$-7.9 \times 10^{-4}$	5.9	$-7.4 \times 10^{-4}$	55.1	$-6.2 \times 10^{-4}$	366.7
1000 nm	$2.5 \times 10^{-3}$	6.1	$8.9 \times 10^{-4}$	35.8	$2.7 \times 10^{-4}$	342.5
<b>1vol%oxMWCNT@TiO<sub>2</sub></b>						
500 nm	$-3.4 \times 10^{-3}$	3.8	$-3.0 \times 10^{-3}$	23.1	$8.4 \times 10^{-4}$	1394.4
700 nm	$2.6 \times 10^{-3}$	3.7	$4.7 \times 10^{-4}$	38.1	-	-
1000 nm	$1.2 \times 10^{-3}$	4.2	$4.7 \times 10^{-3}$	42.8	$9.9 \times 10^{-4}$	901.6
<b>5vol%oxMWCNT@TiO<sub>2</sub></b>						
500 nm	$-1.8 \times 10^{-3}$	3.0	$-1.5 \times 10^{-3}$	21.0	$2.6 \times 10^{-3}$	4192.0
700 nm	$6.3 \times 10^{-3}$	1.0	$1.3 \times 10^{-3}$	10.2	$6.5 \times 10^{-4}$	1479.9
1000 nm	$6.8 \times 10^{-3}$	4.0	$3.5 \times 10^{-3}$	27.2	$7.6 \times 10^{-4}$	408.7



**Figure S6.** Nanosecond laser photolysis transient absorption spectra recorded upon 355 nm excitation ( $\sim 8$  mJ/pulse, 150 fs FWHM) of  $\text{TiO}_2$  nanofibers dispersions in  $\text{D}_2\text{O}$  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 ( $\sim 8$  mJ/pulse, 5 ns (FWHM)) of  $\text{TiO}_2$  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.