Electronic Supplementary Information

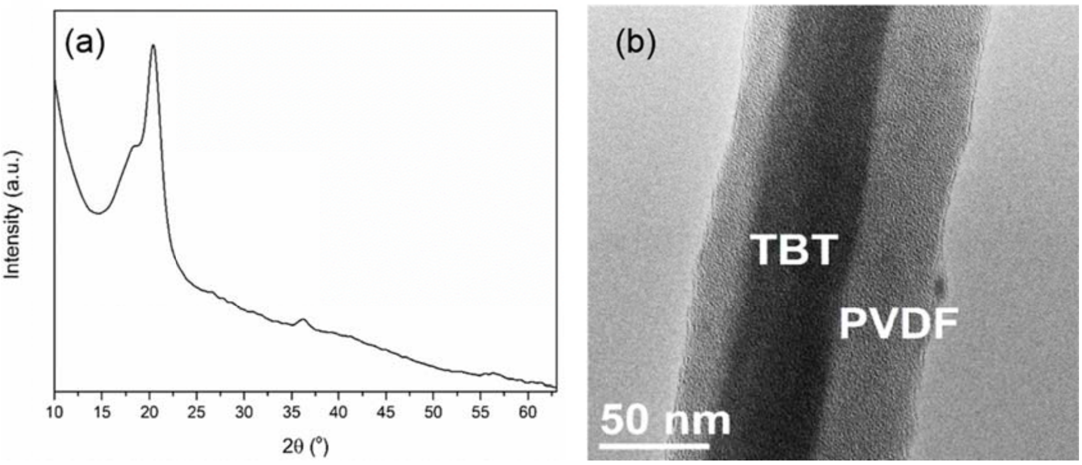

Figure S1. XRD pattern (a) and TEM image (b) of electrospun PVDF–TBT nanofibres prior to hydrothermal treatment.

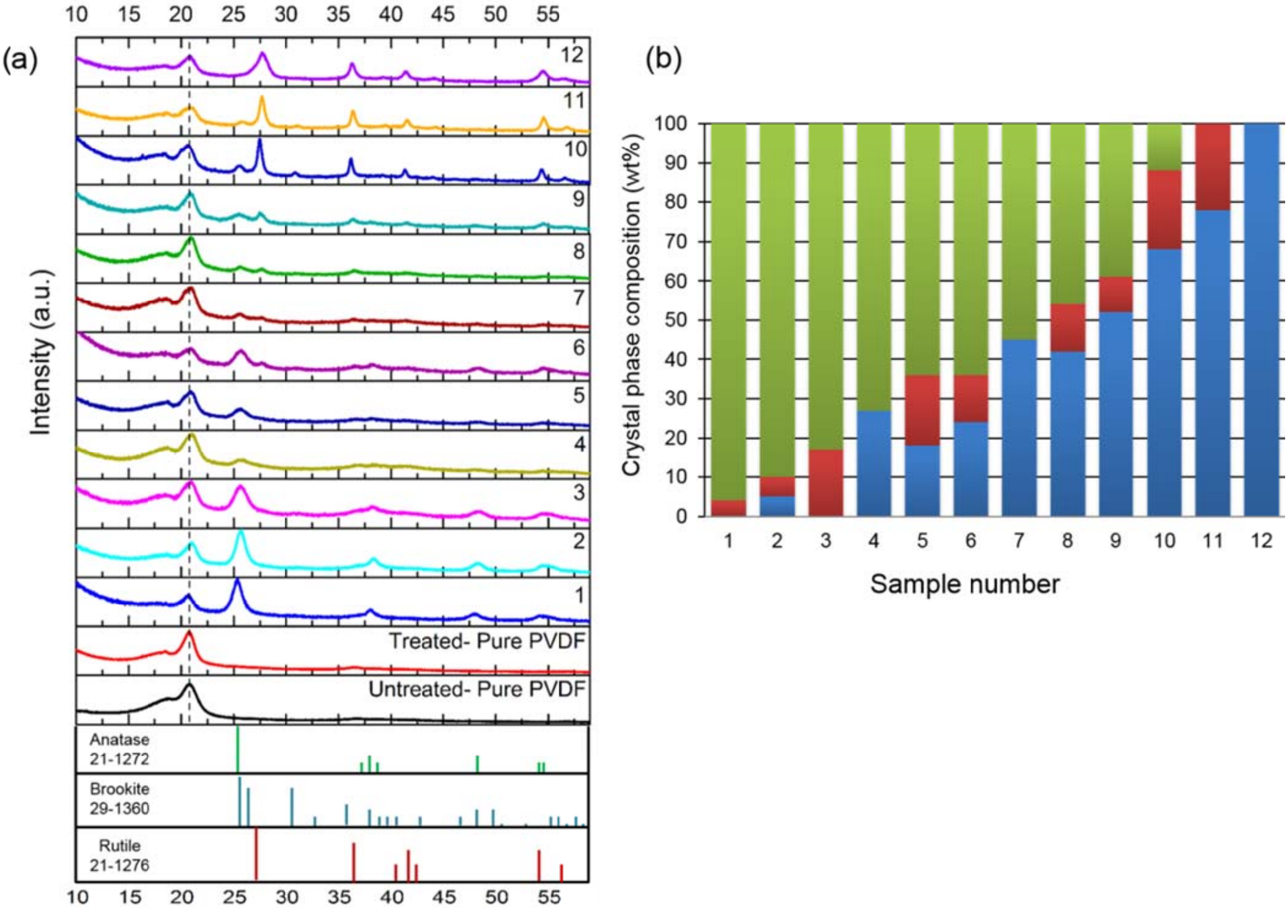

Figure S2. Room temperature PXRD patterns (a) of PVDF before and after hydrothermal treatment as well as the 12 TiO_2–PVDF samples obtained after hydrothermal treatment as labelled on the right of each PXRD pattern. Respective JCPDS card numbers and peak positions of anatase, brookite and rutile phases are indicated at the bottom of the PXRD patterns. Graph of crystal phase composition of the 12 TiO_2-PVDF samples obtained after hydrothermal treatment (b) as labelled.

The peak at ~21° indicated the PVDF phase and no change was observed in this peak after hydrothermal treatment at 120 °C for 24 h.

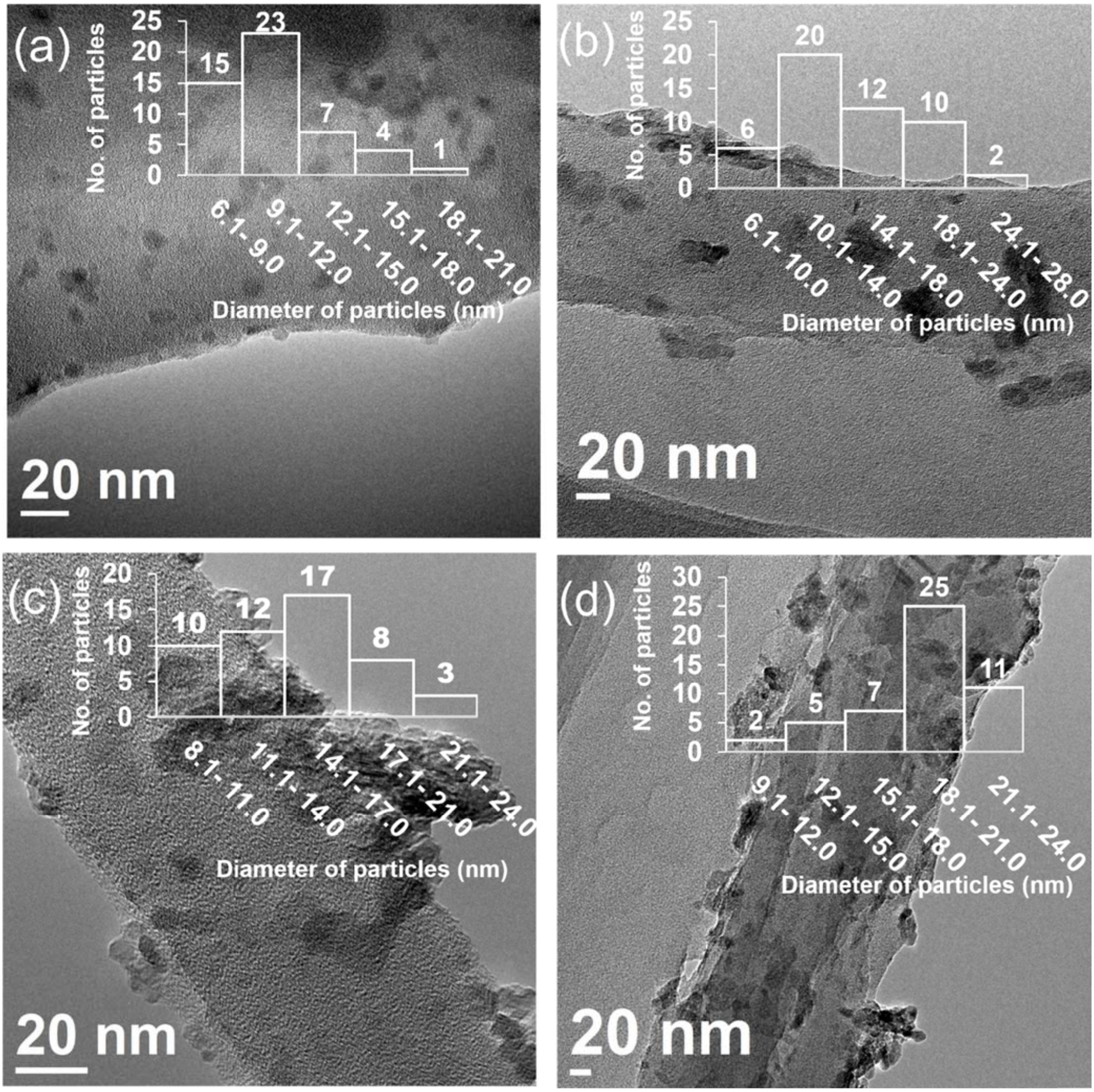

Figure S3. TEM images and size distribution of 50 discrete TiO_2 NPs in a) sample 2, b) sample 3, c) sample 4 and d) sample 5.

Sample No.	Titania Content (%)	PVDF Content (%)
1	28.7	71.3
2	32.3	67.7
3	27.7	72.3
4	27.6	72.4
5	29.9	70.1
6	29.2	70.8
7	32.4	67.6
8	38.1	61.9
9	30.1	69.9
10	32.8	67.2
11	36.5	63.5
12	40.2	59.8

Table S1. Percentage of TiO_2 and PVDF in the PVDF–TiO_2 membranes obtained from TGA analysis.

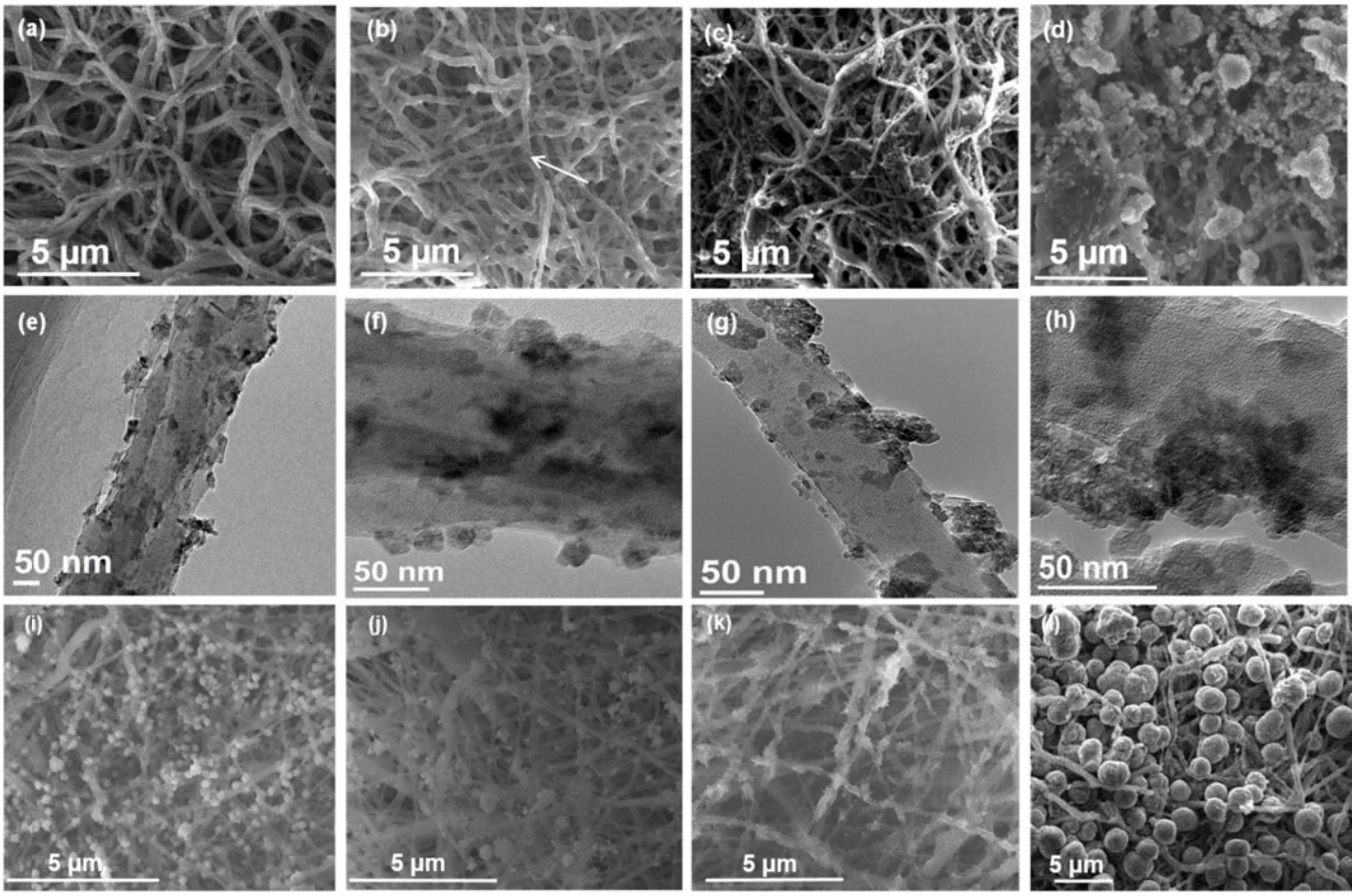

Figure S4. SEM images of PVDF–TiO_2 samples 3–6 (a–d), sample 8 (i) and samples 10–12 (j–l). TEM images of PVDF–TiO_2 electrospun NFs of samples 3–6 (e–h).

TEM images of samples 8 and 10–12 are not shown due to detachment of TiO_2 NPs from the electrospun NFs after sonication as part of the preparation for TEM analysis.

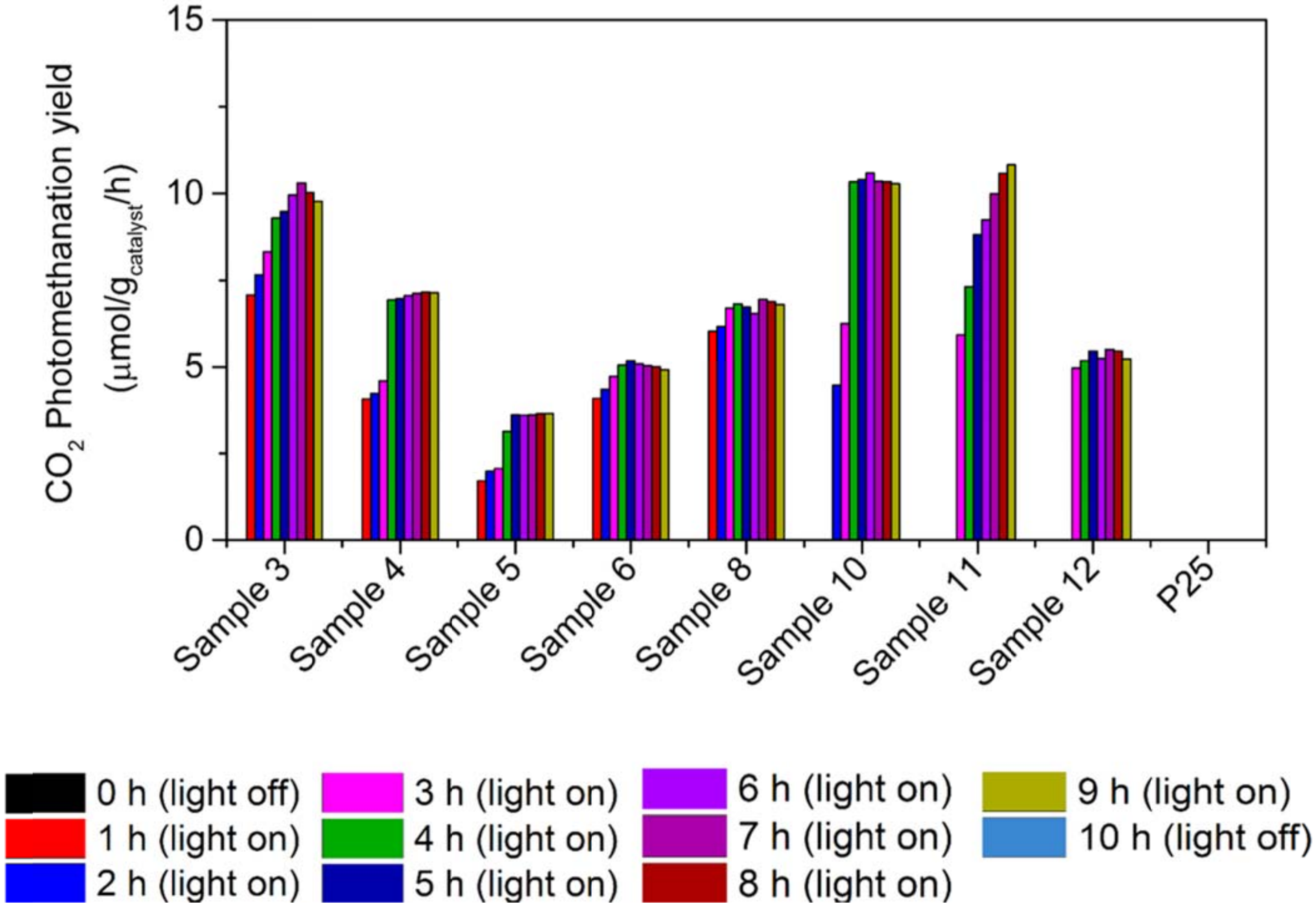

Figure S5. CO_2 photomethanation yield over 11 h under UV irradiation of the PVDF–TiO_2 membranes (samples 3, 4, 5, 6, 7, 10, 11 and 12) and P25.

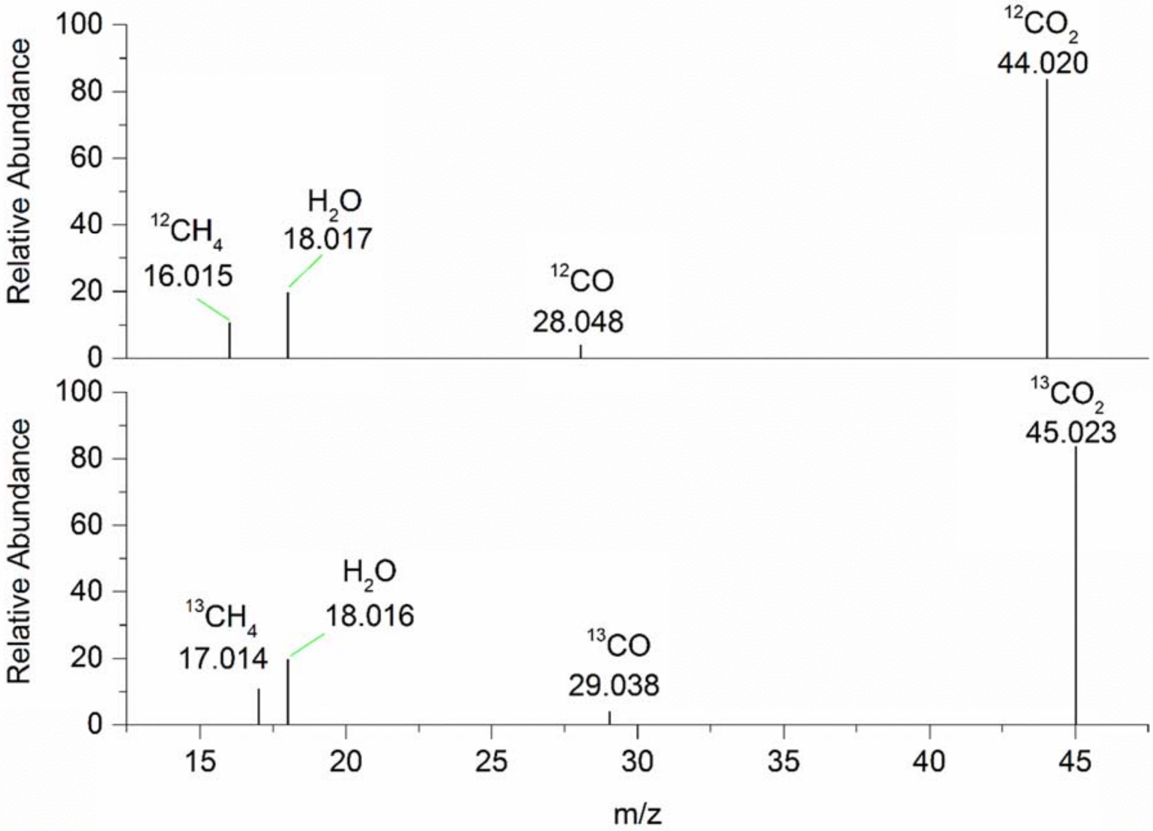

Figure S6. GC–MS spectra of the products of photocatalytic reduction of $^{12}CO_2$ (top) and $^{13}CO_2$ (bottom) over sample 2 under UV irradiation.

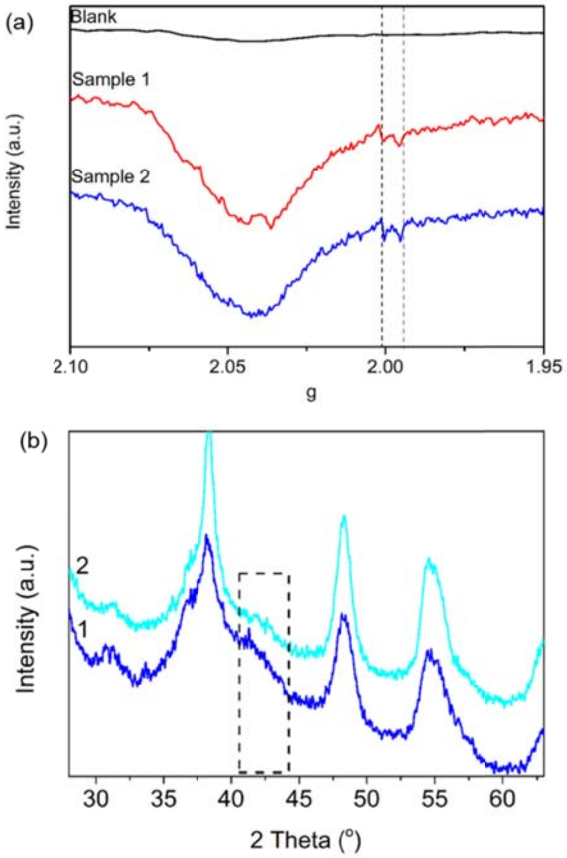

Figure S7. ESR patterns of copper acetate at 77 K without (blank) or with Sample 1 and 2 after irradiation (a). The dashed lines indicate the peak width of Sample 2 at g≈1.99. High resolution room temperature PXRD patterns of Sample 1 and 2 as labelled (b). Sample 2 has been offset up the intensity axis. The dashed rectangle highlights the difference in peak intensities centred at 42.8°.

The emergence of a broad peak centred at 42.8° in the PXRD pattern of Sample 1 is attributed to the formation of various titanium suboxides.[1,2]

References

1. K. Huang, K. Sasaki, R. R. Adzic and Y. Xing, *J. Mater. Chem.*, 2012, **22**, 16824-16832.
2. J. Tang and H. M. Meng, *Phys. Chem. Chem. Phys.*, 2016, **18**, 1500-1506.