Electronic Supporting Information

New insights into polymer mediated formation of anatase mesocrystal

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Materials/Synthesis

Reagents were sourced from the suppliers indicated and were used as received.

General method for the preparation of NH_4TiOF_3 MCs

$(NH_4)_2TiF_6$ (Sigma-Aldrich UK) 0.1 mol L^{-1} poly(ethylene glycol) PEG-6000 (Alfa Chemicals Ltd.) and gelation agent H_3BO_3 (Alfa Chemicals Ltd.) 0.2 mol L^{-1} were dissolved in distilled water (30 mL) under continuous stirring. After full dissolution of the reagents, the resultant gel was kept at 35°C for 20 hours. The resultant precipitate was isolated by centrifugation/decantation and subsequently washed with water (3 x 20 mL) and acetone (3 x 20 mL).

NB. To enable the effect of varying the concentration of PEG-6000 to be evaluated, the following molar ratios of reagents PEG-6000 : $(NH_4)_2TiF_6$: H_3BO_3 were employed, 0 : 4 : 8, 1 : 4 : 8 , 1 : 2 : 4 and 3 : 4 : 8.

General Method for the Preparation of TiO_2 MCs

A sample of NH_4TiOF_3 MCs (ca. 0.5 g) was heated in air at 450 °C for the specified time period (2, 4 or 8 hours). This heating procedure was conducted using a Nabertherm HTCT 03/14 furnace and exhaust gases were vented into a designated fume cupboard (**Caution:** Gaseous HF is liberated in this thermally-mediated transformation).

Characterisation Techniques and Conditions

X-Ray Diffraction (XRD) was conducted on a Bruker D8 Advance system using monochromatic CuKα radiation.

SEM was performed on a Carl Zeiss NVision 40 electron microscope.

TEM was performed on a FEI Tecnai G2 F30 electron microscope with resolution of 0.14nm.

Raman spectroscopy was conducted using a Renishaw inVia Reflex spectrometer with an illumination wavelength of 633 nm.

Thermogravimetric Analysis was conducted using a Perkin-Elmer Thermogravimetric Analyzer Pyris 1. Heating was conducted from room temperature to 800 C with a heating rate increase of 5 °C / min.

BET Low temperature nitrogen adsorption measurements were conducted using an ATX-6 analyzer (Katakon, Russia). Before measurements the samples (30–60 mg weight) were outgassed at 200 ^oC for 30 min under a dry helium flow. Determination of the surface area was carried out by the 5-point Brunauer, Emmett and Teller (BET) method at the relative pressure range of $P/P_0 = 0.05– 0.25$.

Photocatalysis study

Measurements of photocatalytic activity were conducted under irradiation of a suspension of the analyte MC with an Ocean Optics HPX- 2000 deuterium-halogen lamp (the output power is 1.52 mW, as measured in the 200–1100 nm range by an integrated optical power meter) in a cell thermostated at 37 ^{o}C. Spectrophotometric analysis was performed using an Ocean Optics QE65000 spectrometer. All samples were kept in the dark for 45 minutes prior to conducting the degradation study.

SEM Images

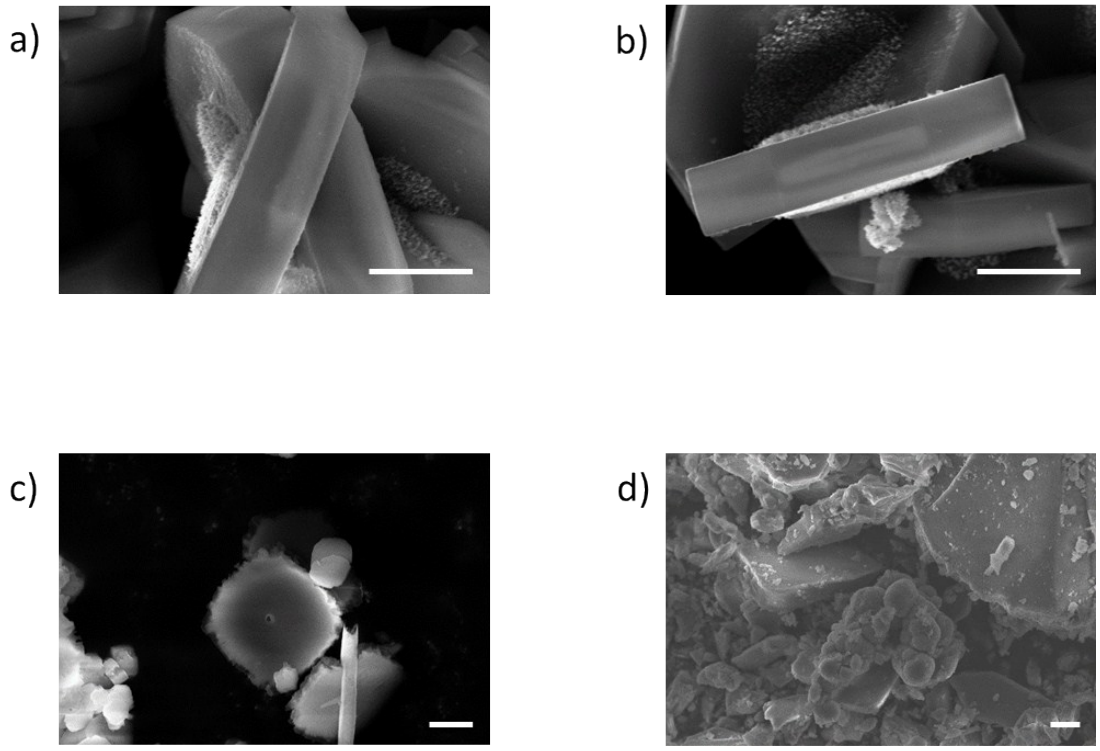

Figure S1 SEM micrographs showing a) NH_4TiOF_3 MCs formed in the presence of too little PEG-6000, showing orientation of the central nanocrystallites; b) a) NH_4TiOF_3 MCs formed in the presence of too little PEG-6000, showing nanocrystallites in the central region on both sides of the larger MC; c) NH_4TiOF_3 MCs formed in the presence of excess PEG-6000 showing defects on the MC surface and central hole; d) NH_4TiOF_3 crystals formed in the absence of PEG-6000. (NB the white scale bars in the bottom right of each SEM micrograph = 1 μm in all cases except Fig S1d where it = 2 μm).

SAED Patterns and TEM/HRTEM Images

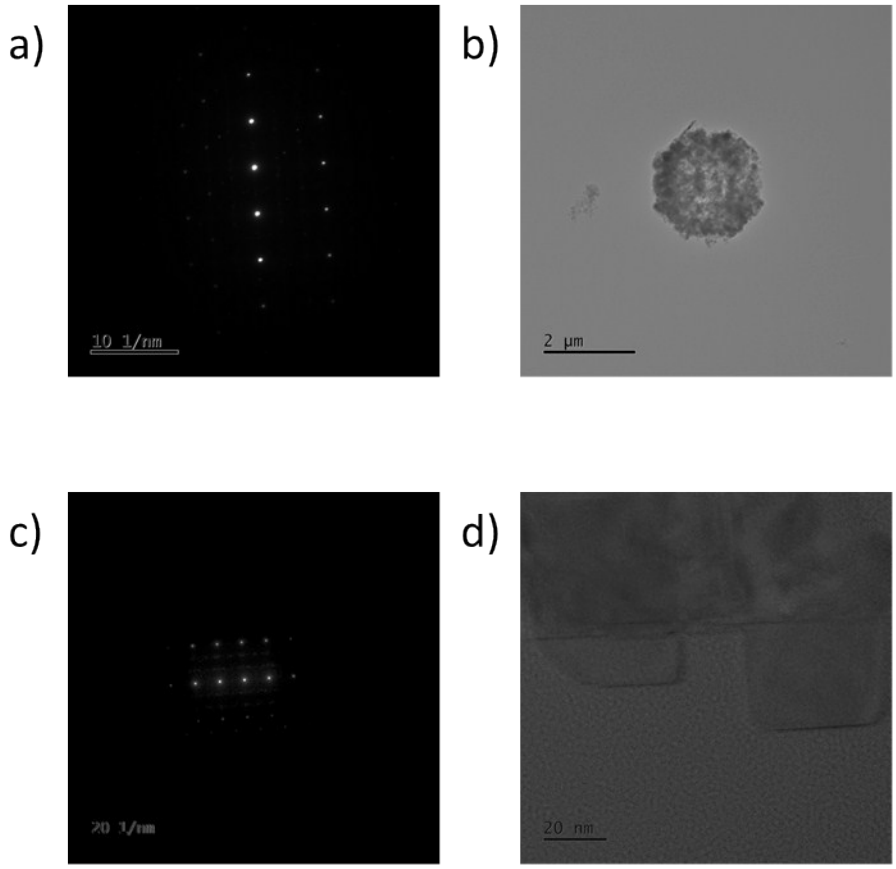

Figure S2 a) SAED pattern and b) TEM micrograph of a TiO_2 MC formed from NH_4TiOF_3 MCs by two hours of heating at 450 °C; c) SAED pattern and d) HRTEM micrograph of the TiO_2 nanocrystals comprising a TiO_2 MC formed from NH_4TiOF_3 MCs by two hours of heating at 450 °C.

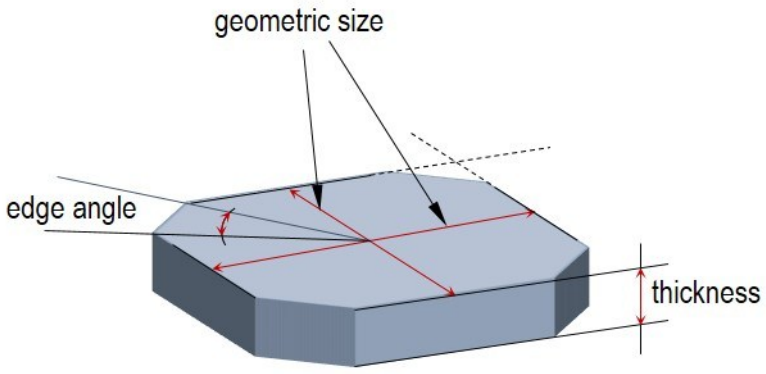

Figure S3 Definition of dimensions reported in Table 2.

Raman Spectroscopy

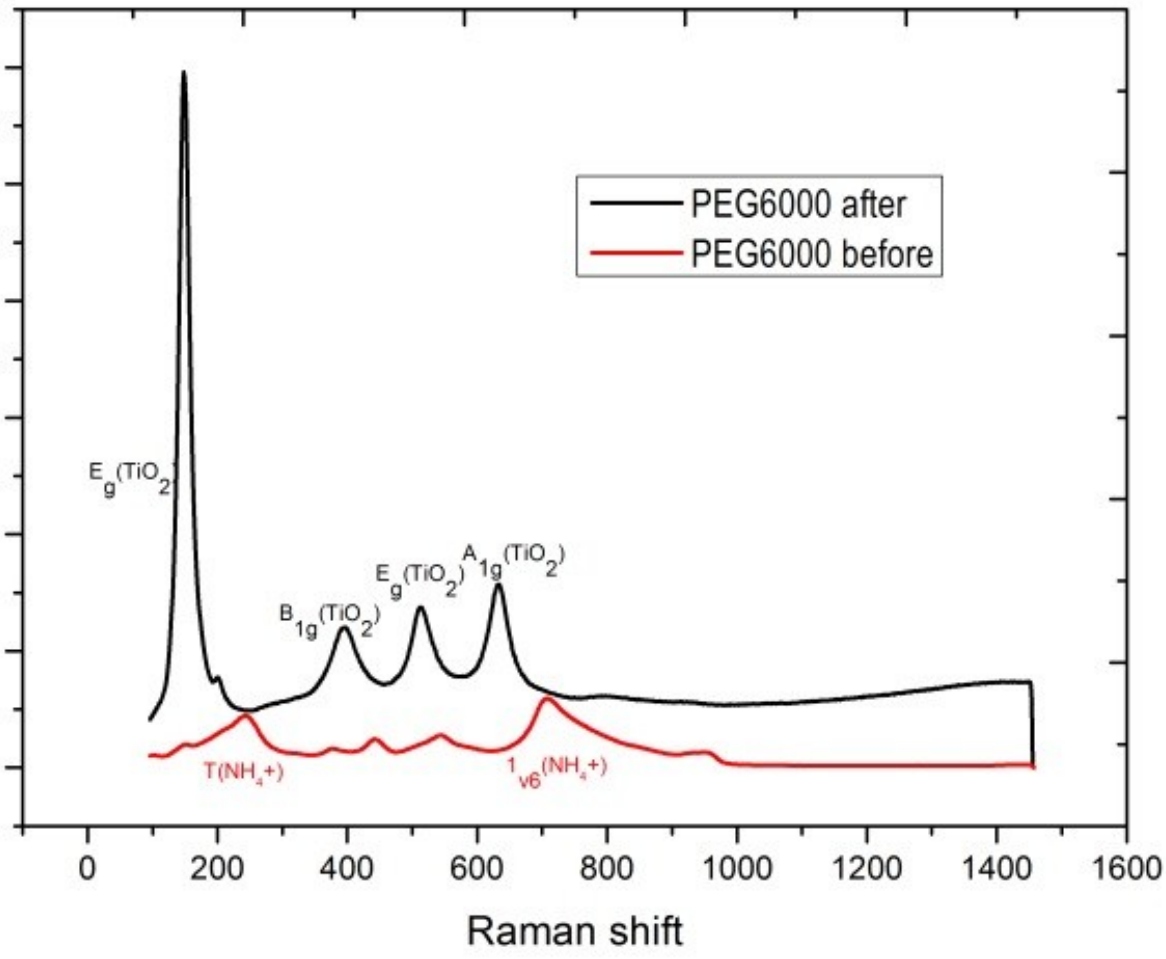

Figure S4 Raman spectrum showing that only anatase TiO_2 is formed during the thermally-mediated transformation of NH_4TiOF_3 MCs into TiO_2 MCs.

FT-IR Spectroscopy

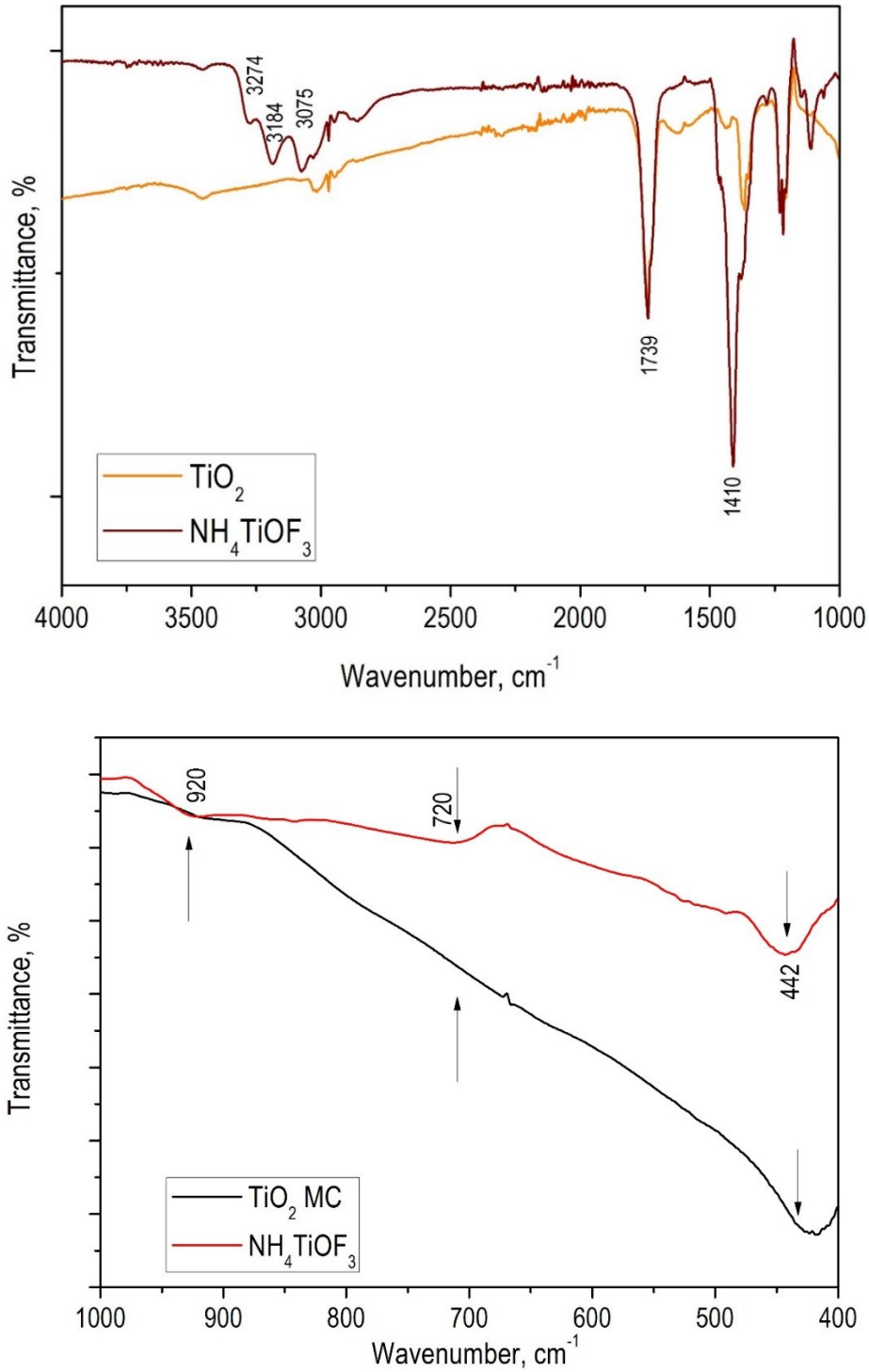

Figure S5 Infrared spectra of NH_4TiOF_3 MCs formed in the presence of PEG-6000 and TiO_2 MCs formed by the thermally-mediated toptactic transformation of these NH_4TiOF_3 MCs after heating at 450 ^oC for 2 hours.

Thermogravimetric Analysis

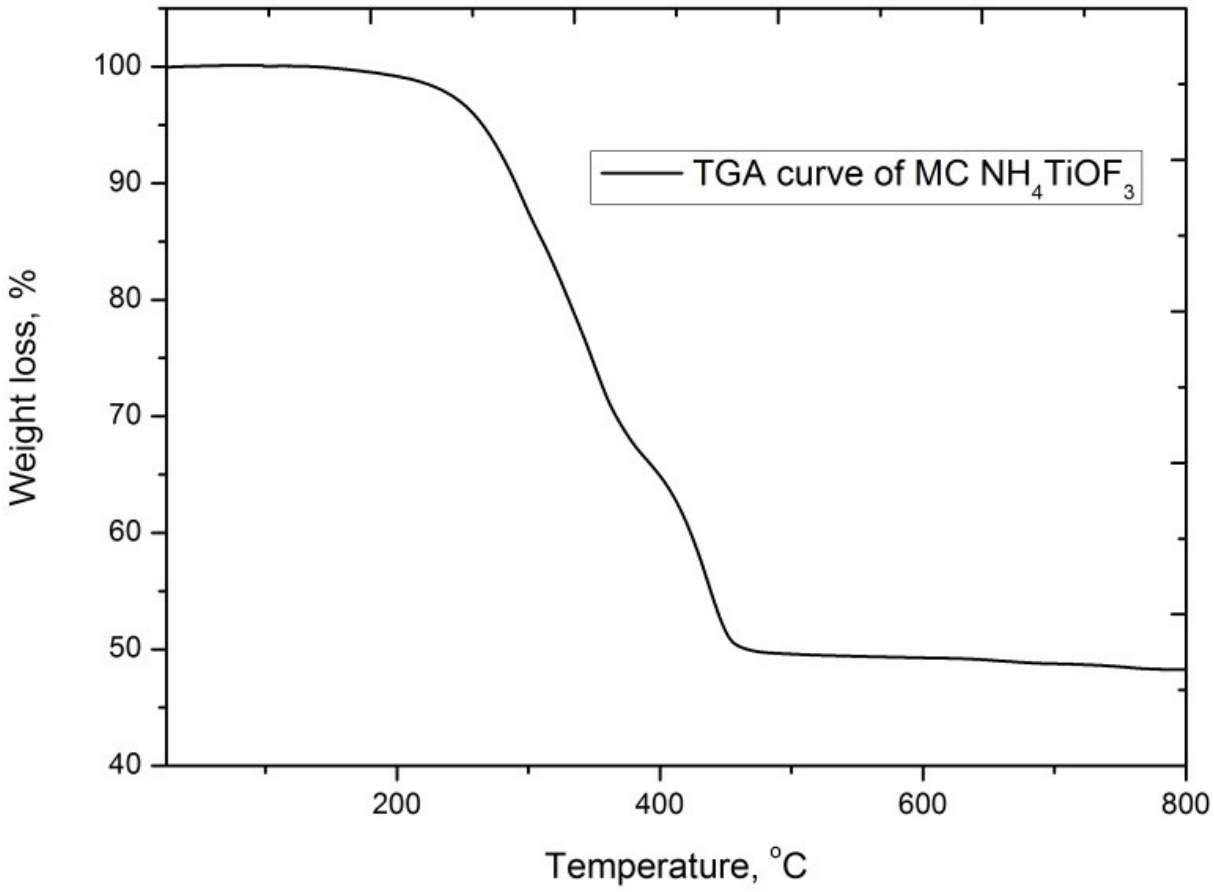

Figure S6 Thermogravimetric analysis profile for NH_4TiOF_3 MCs formed from a 1 : 2 : 4 ratio of PEG-6000 : $(NH_4)_2TiF_6$: H_3BO_3 (RT to 800 °C, heating rate 5 °C / min).

The chemical steps occurring in the formation of the final TiO_2 product can be attributed to the following reactions:[1]

$NH_4TiOF_3 \rightarrow HTiOF_3 \rightarrow TiOF_2 \rightarrow TiO_2$

The mass loss steps can be attributed to the following processes:[1]

Step 1 (25 °C – 250 °C): the impurities such as H_2O and other volatiles are removed.

Step 2 (250 °C – 360 °C): the NH_4TiOF_3 is converted to $HTiOF_3$, through the removal of NH_3 and the $HTiOF_3$ is converted to $TiOF_2$ with loss of HF.

Step 3 (360 °C – 420 °C): Any impurities are removed.

Step 4 (420 °C – 450 °C): $TiOF_2$ is converted to TiO_2.

1 L. D. Zhou, D. Smyth-Boyle and P. O'Brien, *J. Am. Chem. Soc.,* 2008, **130**, 1309

Molar ratio **PEG 6000 : $(NH_4)_2TiF_6$: H_3BO_3**	**Weight Loss (%) and Temperature range of transition (^oC)**			
0 : 4 : 8*	6.1 %		21.9 %	10.6 %
	25-269 ^oC		267-348 ^oC	348-441 ^oC
1 : 4 : 8	7.4 %		21.6 %	11 %
	25-276 ^oC		276-354 ^oC	354-433 ^oC
1 : 2 : 4	11.1 %	14.9 %	7.8 %	16.7 %
	25 – 295 ^oC	295 – 351 ^oC	351 – 388 ^oC	388 – 482 ^oC
3 : 4 : 8	6.3 %	19.7 %	4.7 %	11.1 %
	25 – 260 ^oC	260 – 351 ^oC	351– 381 ^oC	381– 486 ^oC

Table S1 Summary of the data obtained from TGA of the thermally-mediated transformation of NH_4TiOF_3 MCs into TiO_2 MCs.

* in the absence of PEG NH_4TiOF_3 MCs were not formed, instead non-crystallographically-oriented, variously sized crystals of NH_4TiOF_3 were formed (Fig. S1d) which unlike their MC counterparts only gave three transitions in their TGA profile under identical TGA conditions to the NH_4TiOF_3 MCs.

Size distribution

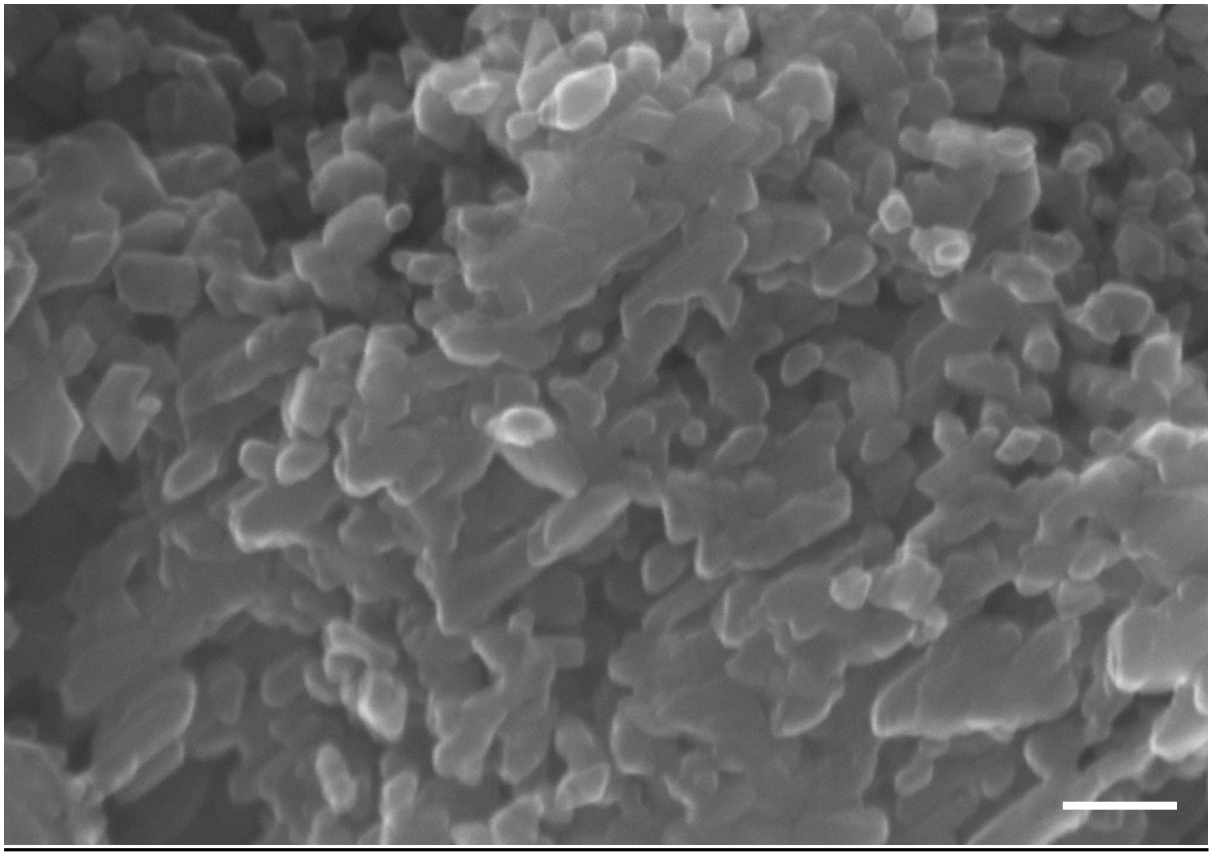

Figure S7 Size distribution of TiO_2 MCs, formed after heating NH_4TiOF_3 MCs for 2 hours, obtained from analysis of the accompanying SEM micrograph (white sizing bar, bottom right = 100 nm) using ImageJ image processing and analysis software (https://imagej.nih.gov/ij/index.html).

X-Ray Diffraction

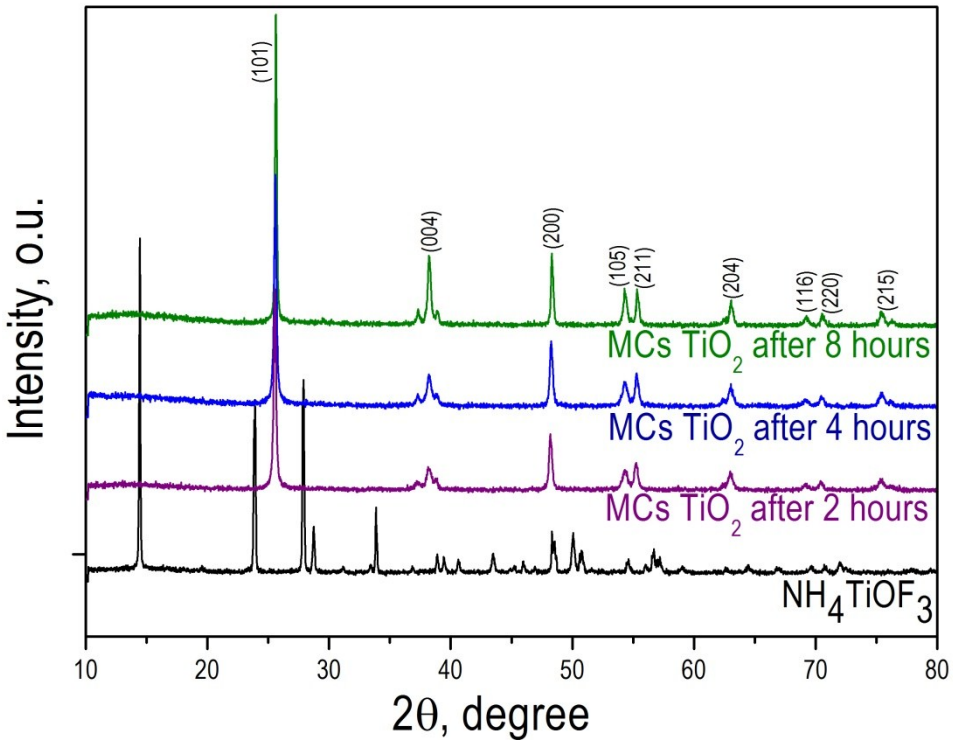

Figure S8 XRD patterns of the first formed NH_4TiOF_3 MCs and the TiO_2 MCs formed from the thermally-mediated transformation of NH_4TiOF_3 MCs after 2, 4 and 8 hours of annealing.

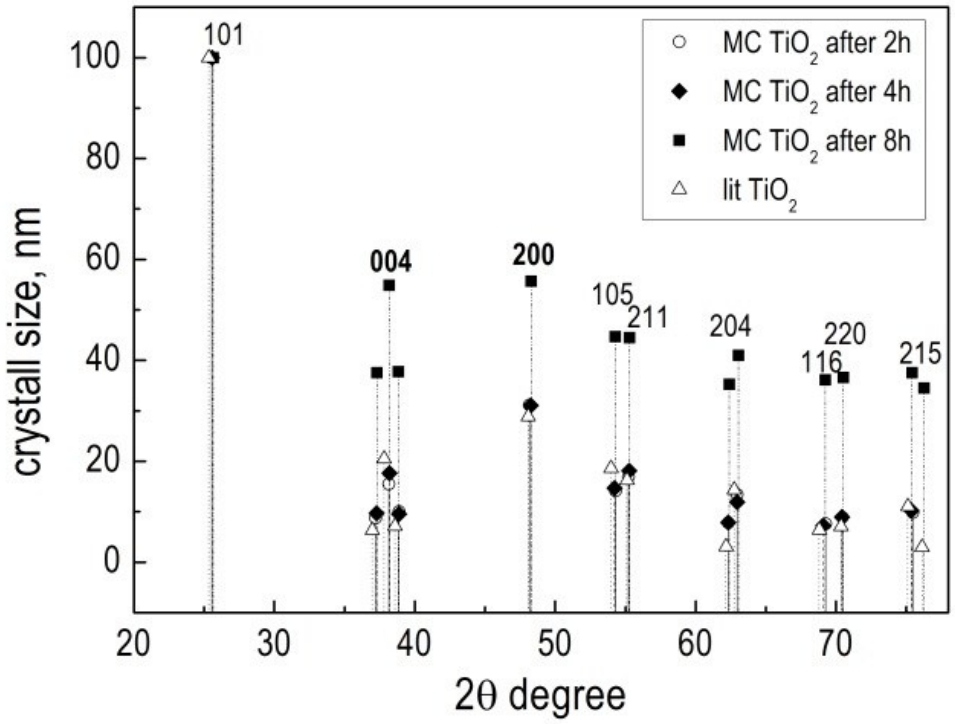

Figure S9 Normalized p-XRD patterns of the MC of TiO_2 generated in this study compared to literature[2] TiO_2.

2 C. J. Howard, T. M. Sabine and F. Dickson, *Acta Crystallographica* B, 1991, **47**, 462.

Anneal time / h	a (expt)[3]	c(expt)[3]	a(lit)[4]	c(lit)[4]
2.000	3.767	9.446	3.785	9.514
4.000	3.758	9.435	3.785	9.514
8.000	3.758	9.435	3.785	9.514

Table S2 Summary of experimentally derived[3] a and c cell parameters for TiO_2 MCs and comparison with published values[4] for anatase.

3 Calculated using XPOW Copyright 1993 see R. T. Downs, K. L. Bartelmehs, G. V. Gibbs and M. B. Boisen *Am. Mineral.*, 1993, **78**, 1104.

4 R. W. G. Wyckoff *Crystal Structures*, Second edition; Interscience Publishers, New York, USA, 1963, **1**, 239-444.

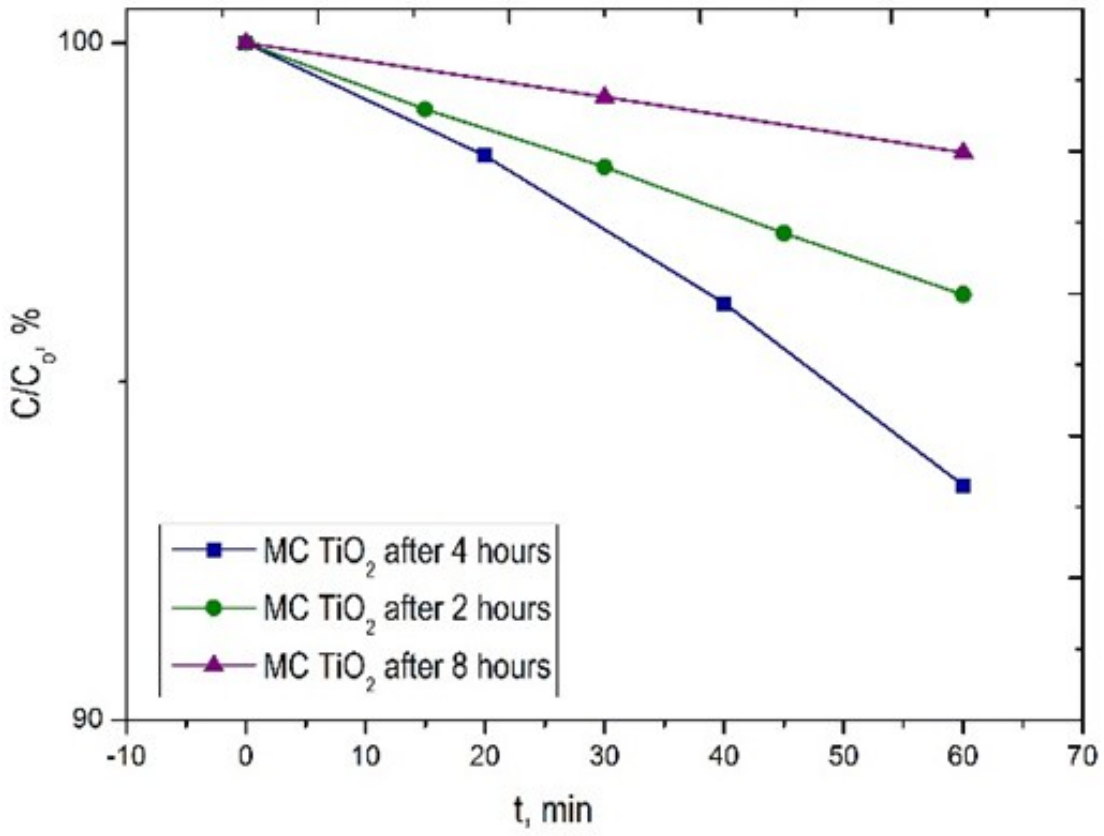

Figure S10 Graph showing the photodegradation profiles obtained for samples of TiO_2 MCs formed from NH_4TiOF_3 MCs after heating for 2 hours (green line), 4 hours (blue line) and 8 hours (purple line) with sizes of between several and tens of nanometres.