Electronic Supplementary Information

Monodisperse Anatase Titania Microspheres with High-thermal Stability and Large Pore Size (~80 nm) as Efficient Photocatalysts

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Fig. S1 Experimental set-up for evaluating photocatalytic performance of the titania materials investigated in this study. A dichroic mirror (66226, Oriel) was installed above the jacked beaker to vertically deliver UV light (280 $<\lambda<400$ nm) onto the reaction mixture. The UV radiation intensity at the surface of the suspension was 16.7 ± 0.2 mW cm⁻².



Fig. S2 Low magnification SEM images of (a) the monodisperse titania microspheres (MTS) solvothermally treated at 220 °C in the presence of 4.5 wt.% ammonia solution and the MTS after calcination at (b) 800 °C, (c) 900 °C, and (d) 1000 °C in air. SEM images were taken without metal sputter coating of the samples.



Fig. S3 High magnification SEM image of the monodisperse titania microspheres solvothermally treated at 220 °C in the presence of 4.5 wt.% ammonia solution and calcined at 1000 °C in air. SEM image was taken without metal sputter coating of the sample.



Fig. S4 Histogram of the size distribution of the monodisperse titania spheres solvothermally treated at 220 °C in the presence of 4.5 wt.% ammonia solution (a) and then calcined at 800 °C (b), 900 °C (c), and 1000 °C (d) in air.



Fig. S5 Raman spectrum of the monodisperse titania spheres solvothermally treated at 220 °C in the presence of 4.5 wt.% ammonia solution then calcined at 900 °C for 2 h in air.



Fig. S6 XRD patterns of the Degussa (Evonik) P25 nanoparticles as obtained and after calcination at temperatures ranging from 500 to 900 °C for 2 h in air. A = Anatase and R = Rutile phase titania.



Fig. S7 XRD patterns of the amorphous precursor spheres (APS) and after calcination (without solvothermal treatment) at temperatures ranging from 500 to 800 °C for 2 h in air. A = Anatase and R = Rutile phase titania.



Fig. S8 UV-vis diffuse reflectance spectra of MTS (a) and P25 (c) calcined at varying temperatures for 2 h in air, and the relationship between the transformed Kubelka-Munk function versus the photon energy (b and d) for each material. In (b) and (d), a straight line tangential to the slope was extended to cut the horizontal axis to obtain the band gap energy of the titania samples.¹⁻³



Fig. S9 XPS survey spectra of the MTS sample before and after washing with ethanol (a) and high-resolution N1s XPS spectra (b) of the MTS before washing, MTS washed using ethanol, MTS-800 °C and MTS-900 °C as labelled (the spectra of the MTS washed using ethanol, MTS-800 °C and MTS-900 °C sample were shifted up the vertical axis by 500, 900 and 1200 CPS, respectively).

The X-ray photoelectron spectrometer (XPS) data were recorded on a VG ESCALAB 220i-XL spectrometer (UK) equipped with a twin crystal monochromated Al K_{α} X-ray source, which emitted a photon energy of 1486.6 eV at 10 kV and 22 mA. Samples were secured onto Al holders and were measured in the analysis chamber at a typical operating pressure of ~7×10⁻⁹ mbar. An electron flood gun was used to compensate the charging effect of non-conductive materials. Spectra were obtained at a step size of either 1.0 eV (survey scans) or 0.05 eV (regional scans). Quantification and curve fitting of XPS spectra were performed using CasaXPS software. The C1s peak at 285.0 eV was used as a reference for the calibration of the binding energy scale.



Fig. S10 (a) Arrenhius plot of $ln(A_R/A_0)$ vs 1/T for activation energy calculations according to a previously reported method.⁴ (b) XRD patterns of the MTS calcined at varied temperatures for 2 h (as indicated) in air.



Fig. S11 TEM images (a and c) and equivalent crystal size distribution (b and d) of the MTS solvothermally treated at 220 °C in the absence of ammonia (a and b) and those in the presence of 4.5 wt% ammonia solution (c and d). Note: The average crystal size was estimated by assuming $\frac{5}{5}$

all the particles have a spherical shape. The crystal diameter, D, is given by the equation: $D=2\sqrt{\pi}$, where S is the area of the nanocrystal measured using Image J software and π is 3.14.



Fig. S12 TEM images (a, b) of the ultramicrotomed MTS-4.5 wt% sample showing the faceted anatase nanocrystals are bipyramid crystals, with $\{101\}$ (side) and $\{001\}$ (top) facets exposed. A drawing (c) of a truncated bipyramid anatase crystal is given to indicate the location of $\{101\}$ and $\{001\}$ facets.

The reported surface energy values of the {101} and {001} facets are 0.44 J m⁻² and 0.90 J m⁻², respectively.⁵ To reduce the surface energy during the crystal growth, the resulting anatase nanocrystals will grow in size gradually minimising the exposure of high energy {001} facets and therefore leading to the final anatase crystals showing a truncated bipyramid crystal habit. This result is in good agreement with previous papers.^{6,7}



Fig. S13 SEM images of the monodisperse titania spheres solvothermally treated at 220 °C in the presence of 0 (a1 and a2), 4.5 (b1 and b2) and 17.4 wt.% (c1 and c2) ammonia solution and these samples calcined at 800 °C (a3, b3 and c3), 900 °C (a4, b4 and c4), and 1000 °C (a5, b5 and c5). SEM images were taken without metal sputter coating of the samples.



Fig. S14 XRD patterns of the titania microspheres solvothermally treated at 220 °C in the presence of 17.4 wt.% ammonia solution and calcined at diverse temperatures ranging from 800 to 1000 °C for 2 h in air. A = Anatase and R = Rutile phase titania.



Fig. S15 (a) Time profile of methylene blue (MB) absorbance spectrum and (b) corresponding photodegradation of MB (rate constant: $k=0.001 \text{ min}^{-1}$) observed in the absence of photocatalyst under UV light irradiation. The amount of MB photodegraded was obtained by calculating the change of concentration (C/C₀) from the variation of absorbance (A/A₀) at 665 nm. C₀ and A₀ denote initial concentration and absorbance of MB, respectively.



Fig. S16 SEM image of the MTS-4.5 wt%-800 °C sample after the photocatalytic test.

This sample retains its spherical morphology, the nanoparticles on the outer surfaces come from partial damage to the surface layer of the titania microspheres as a result of the continuous stirring during the photocatalytic reaction. These results suggest that the sample has good mechanical stability due to the sintering at high temperature (> 800 °C).



Fig. S17 Comparison of the apparent rate constants for the photocatalytic reactions employing the MTS samples prepared in the presence of different ammonia concentrations and subsequently calcined at 900 °C in air.

Table S1. Phase content and physical properties of the MTS samples calcined at 900°C in all.			
Sample name	Rutile content (wt.%)	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
MTS-0 wt.% -900 °C	19.6	2.5	0.023
MTS-4.5 wt.% -900 °C	0	10.9	0.123
MTS-17.4 wt.% -900 °C	2.8	6.4	0.061

Table S1. Phase content and physical properties of the MTS samples calcined at 900 °C in air.

Specific surface area obtained from adsorption data in the P/P_0 range from 0.05 to 0.20. Pore volume calculated from the adsorption branch at $P/P_0=0.98$.

Both the MTS-0 wt.% -900 °C and MTS-17.4 wt.% -900 °C sample had a mixed phase titania composition and they had lower specific surface area and porosity than the MTS-4.5 wt.% -900 °C sample. The photocatalytic activities of the MTS-0 wt.% -900 °C and MTS-17.4 wt.% -900 °C samples were inferior to that of MTS-4.5 wt.% calcined at same temperature due to their much reduced specific surface area and porosity, and relatively larger crystal sizes (Shown in Fig. S13 a4, b4 and c4).

References

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