

Supplementary Information

Tunable composition aqueous-synthesized mixed-phase TiO₂ nanocrystals for photo-assisted water decontamination: comparison of anatase, brookite and rutile photocatalysts

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TiO₂ synthesis

Table S 1 summarizes the synthesis conditions in terms of agitation speed, temperature, residence time and pH in tailoring the mixed-phase composition of nanoTiO₂ particles. Table S 2 shows the reproducibility of the composition of the triplicate synthesis runs of the mixed-phase nanoTiO₂.

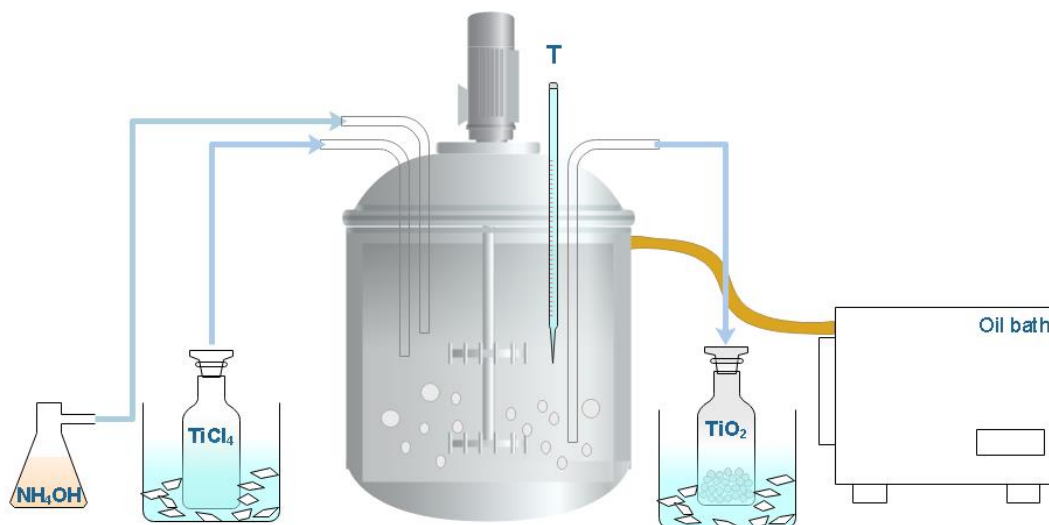
Table S 1 Synthesis conditions favoring mixed-phase TiO₂ of variable composition

Parameter Test No	A _b	101	100	B _r	107	R _b
Feed solution TiCl ₄	0.1 M	0.1 M	0.1 M	0.1 M	0.1 M	0.5 M
Temperature	80 °C	80 °C	80 °C	80 °C	80 °C	80 °C
Residence time	30 min	30 min	60 min	60 min	30 min	30 min
Agitation	800 rpm	800 rpm	800 rpm	400 rpm	400 rpm	400 rpm
pH _{steady-state}	pH 2	pH 1	0.7-0.8	0.7-0.8	0.7-0.8	<0.5
Base	NH ₄ OH	NH ₄ OH	No	No	No	No
Phase Composition Based on XRD Data						
Anatase	69 ±1	45	15	12 ±2	20	-
Brookite	31 ±1	35	65	63 ±1	60	37 ±2
Rutile	-	20	25	25 ±1	65	63 ±2

Table S 2 Reproducibility of the composition of the synthesized mixed-phase nanoTiO₂ materials

Parameter Test No	A _b			B _r			R _b		
Feed solution [TiCl ₄]	0.1 M			0.1 M			0.5 M		
Temperature	80 °C			80 °C			80 °C		
Residence time	30 min			60 min			30 min		
Agitation	800 rpm			400 rpm			400 rpm		
pH	pH 2			0.7-0.8			<0.5		
Base	NH ₄ OH			No			No		
Phase Composition Based on XRD Data									
Anatase	70	68	70	10	15	12	-	-	-
Brookite	30	32	30	65	62	62	35	41	36
Rutile	-	-	-	25	23	26	65	59	64
*Steady state pH~; #Steady-state pH<0.5									

The continuous stirred tank reactor set up can be seen in Schematic S 1.



Schematic S 1 Synthesis of TiO_2 in continuous stirred tank reactor by forced hydrolysis of aqueous TiCl_4 solution

The synthesis process flowchart of the mixed-phase nano TiO_2 is shown in Figure S 1.

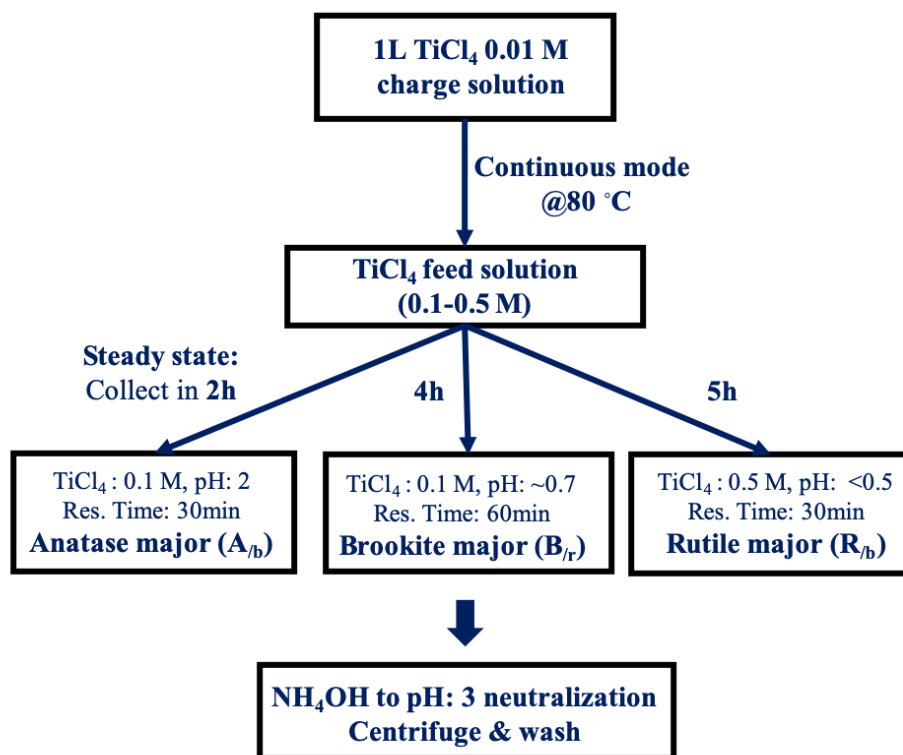


Figure S 1 Flowchart of synthesis of mixed-phase TiO_2 nanoparticles

SEM Images

Figure S 2 shows the SEM images for the three mixed-phase TiO₂ NPs and compared with P25.

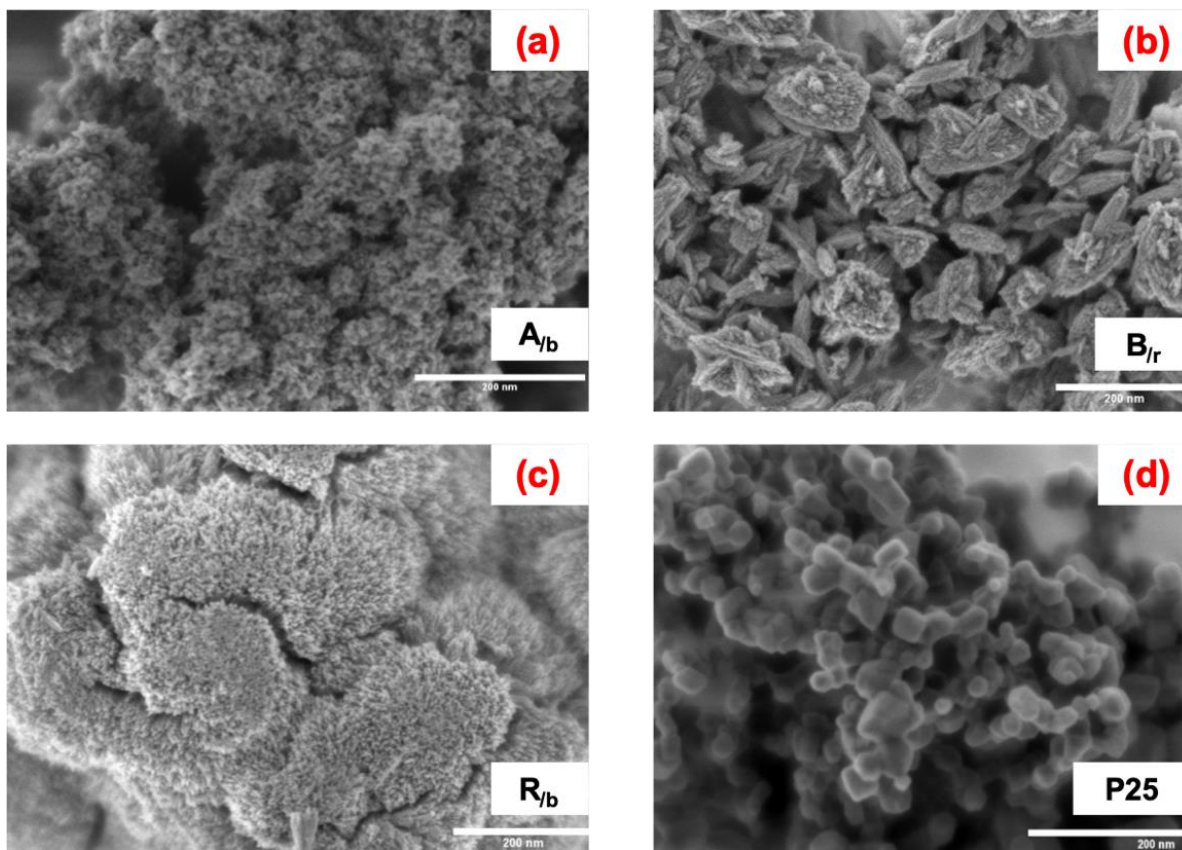


Figure S 2 SEM images of synthesized TiO₂ nanoparticles; (a) anatase major, **A_b**, (b) brookite major, **B_r**, (c) rutile major, **R_b**, and (d) commercial P25

TEM Images

The HM-TEM images of the three mixed-phase nanoTiO₂ materials are analyzed with the DigitalMicrograph software to substantiate the co-existence of two phases in the nanograined particles. Lattice profiles were taken at three areas (2-3 nm spots) of each image featuring nanograined particles and characteristic d-spacings are identified. More specifically, in the image of Figure S 3 of the **A_b** titania we identified the A(101), A(004), A(200) and B(121) and B(120) planes within 2-3 nm space confirming the mixed-phase **A_b** character of this material. In Figure S 4 featuring an image from the **B_r** material we have B(121), B(120), B(111) and R(111) planes confirming the mixed-phase **B_r** character of this material. Finally, in Figure S 5 we have identified the R(110), R(101) and B(032) planes, which correspond for the **R_b** mixed-phase composition.

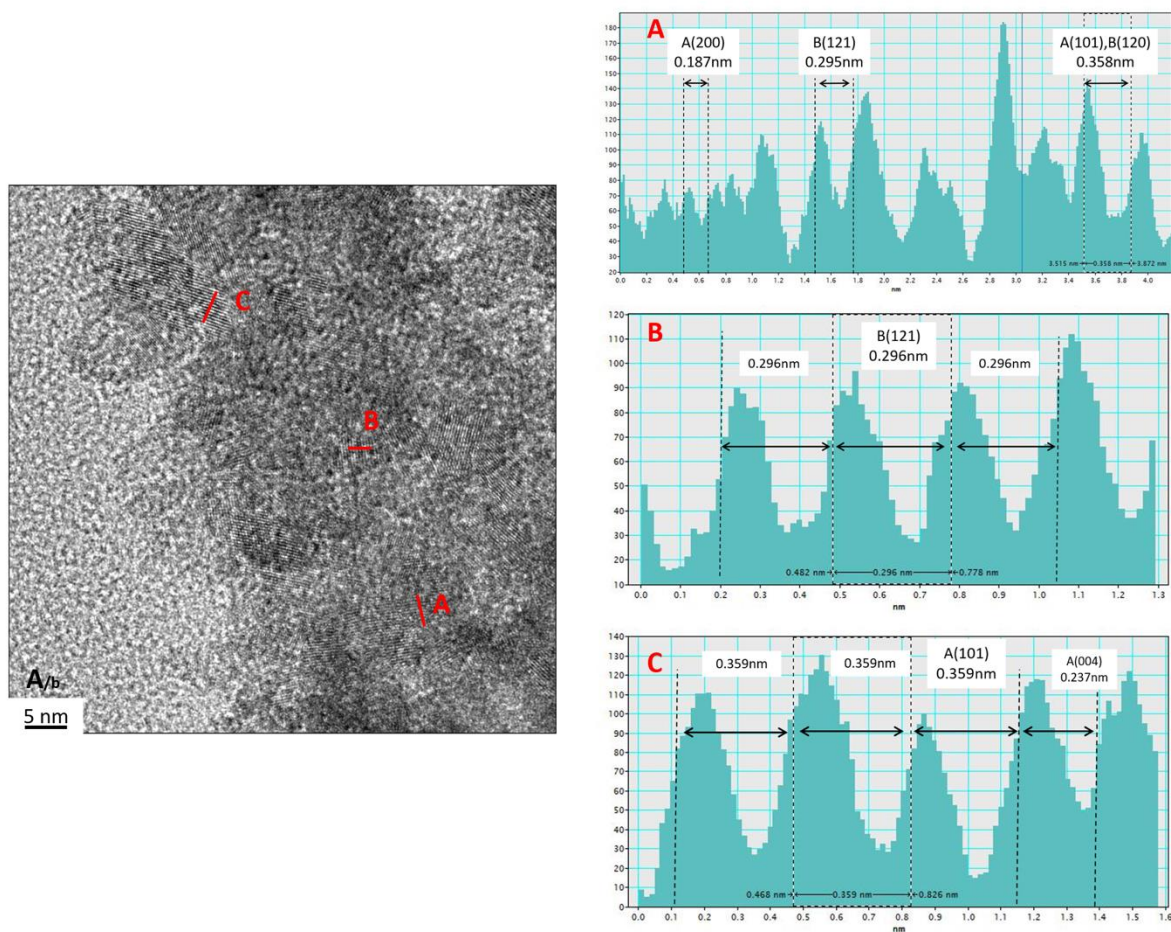


Figure S 3 High resolution TEM image of nanograined particles of the mixed-phase A_b nanoTiO₂ photocatalyst with d-spacing lattice profiles at three explored areas

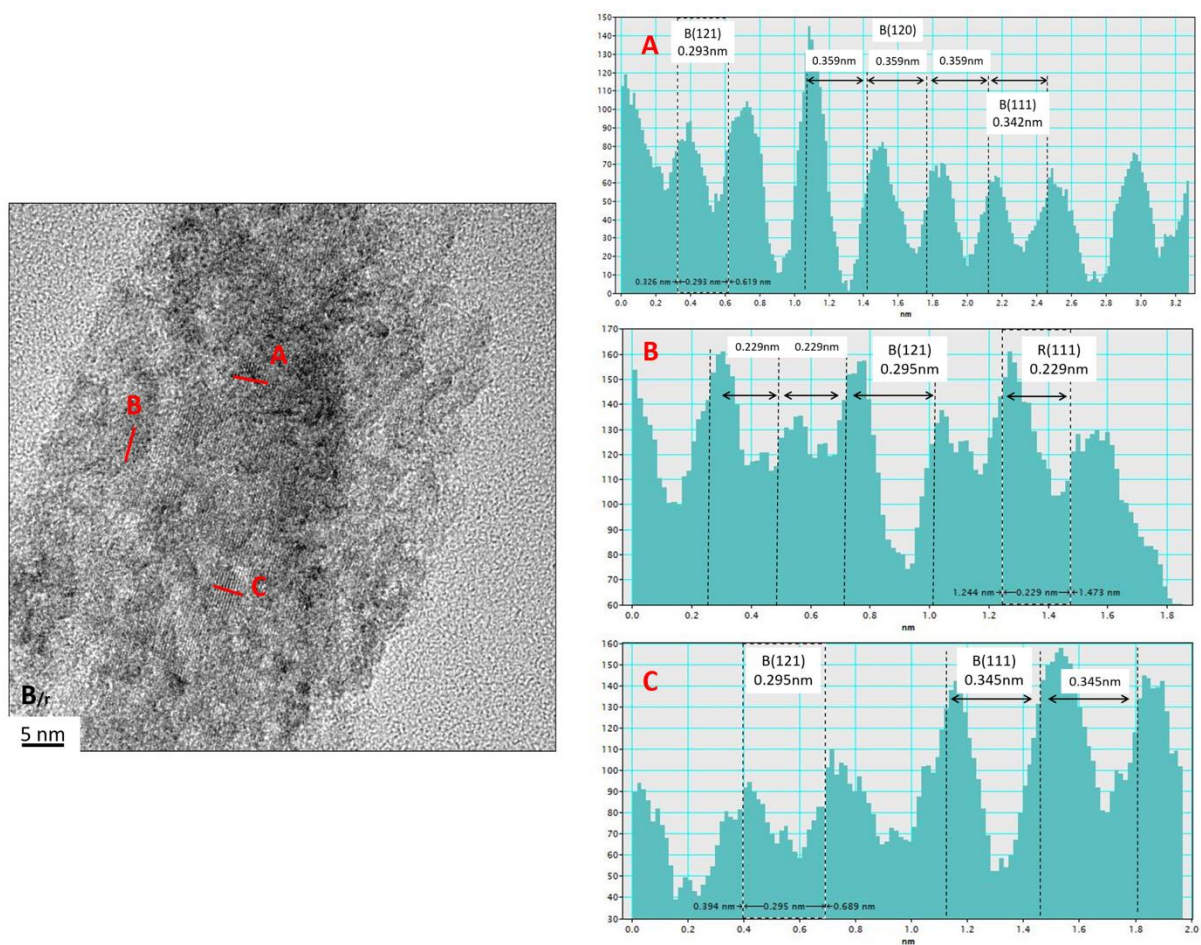


Figure S 4 High resolution TEM image of nanograined particles of the mixed-phase B_r nanoTiO₂ photocatalyst with d-spacing lattice profiles at three explored areas

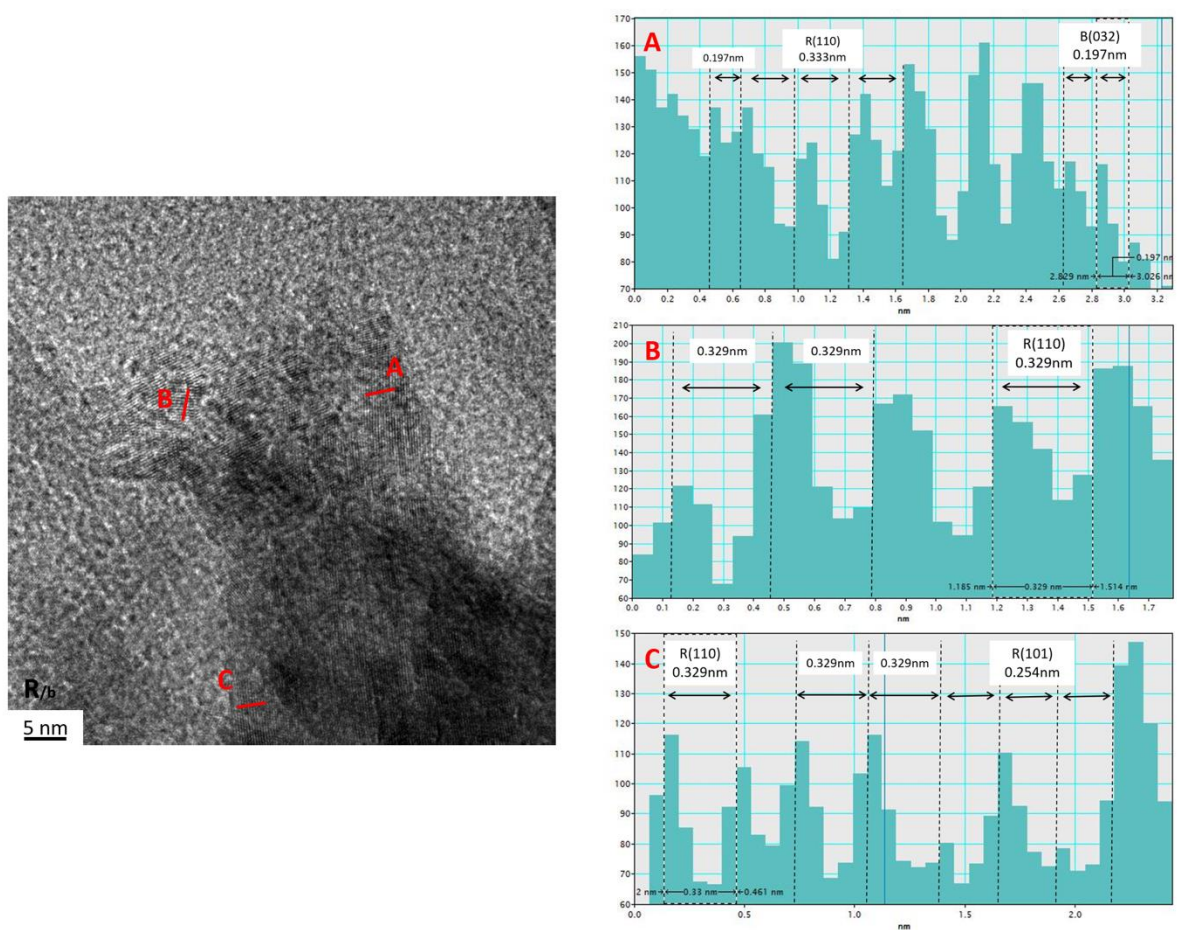


Figure S 5 High resolution TEM image of nanograined particles of the mixed-phase R/b nanoTiO₂ photocatalyst with d-spacing lattice profiles at three explored areas

BET data

Figure S 6 shows the Brunauer-Emmett-Teller (BET) method isotherms for the three mixed-phase TiO₂ NPs and compared with P25. The pore size distribution was determined using the Barret-Joyner-Halender (BJH) method via the adsorption branch of the isotherm, see Figure S 6(insets).[1]

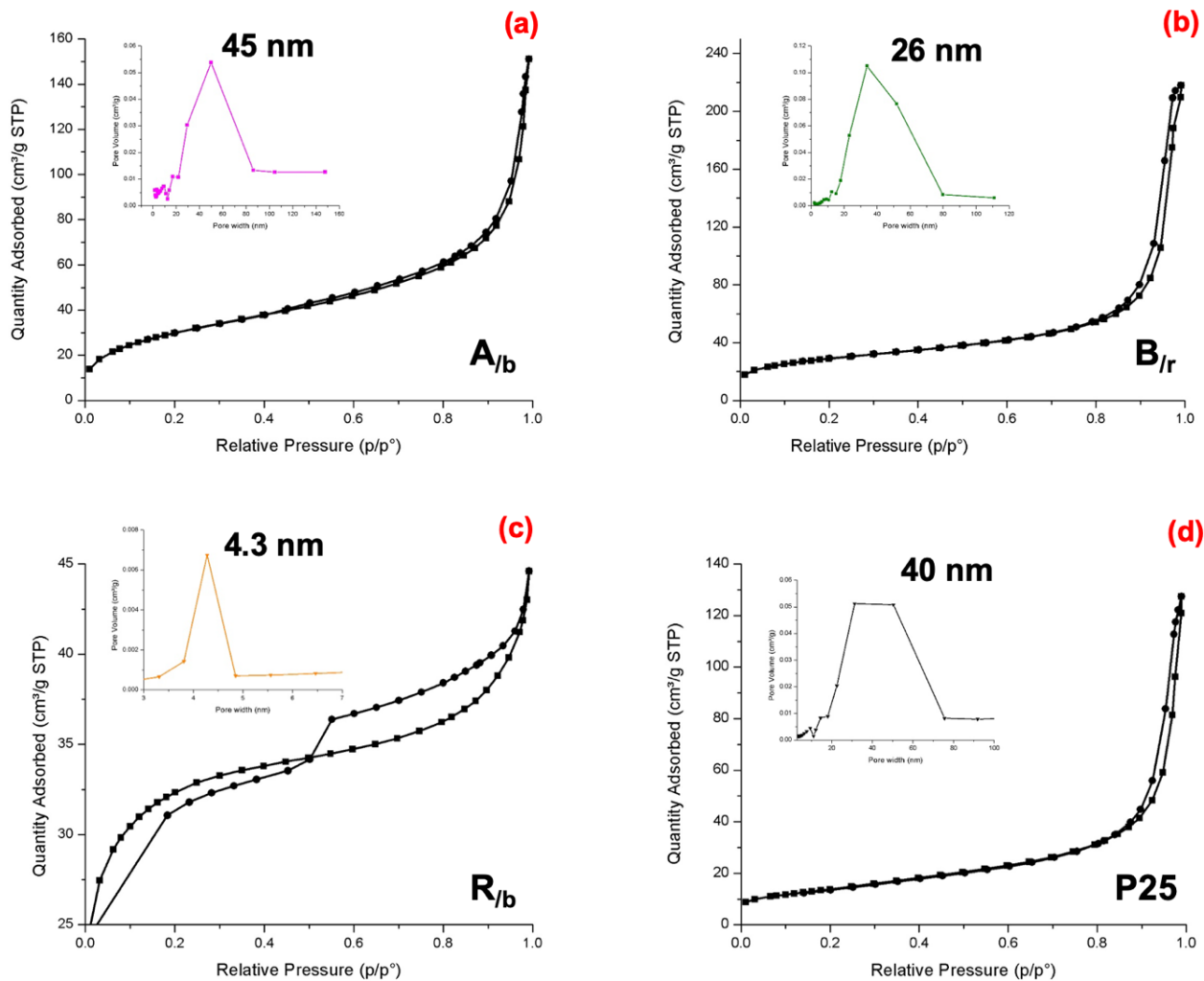


Figure S 6 N_2 adsorption-desorption BET isotherms of synthesized TiO_2 nanoparticles (a) anatase major, A/b , (b) brookite major, B/r , (c) rutile major, R/b , and (d) commercial P25; insets show the BJH pore size distributions

Raman spectra

Figure S 7 shows the Raman spectra for the three mixed-phase TiO₂ NPs with their characteristic peaks.

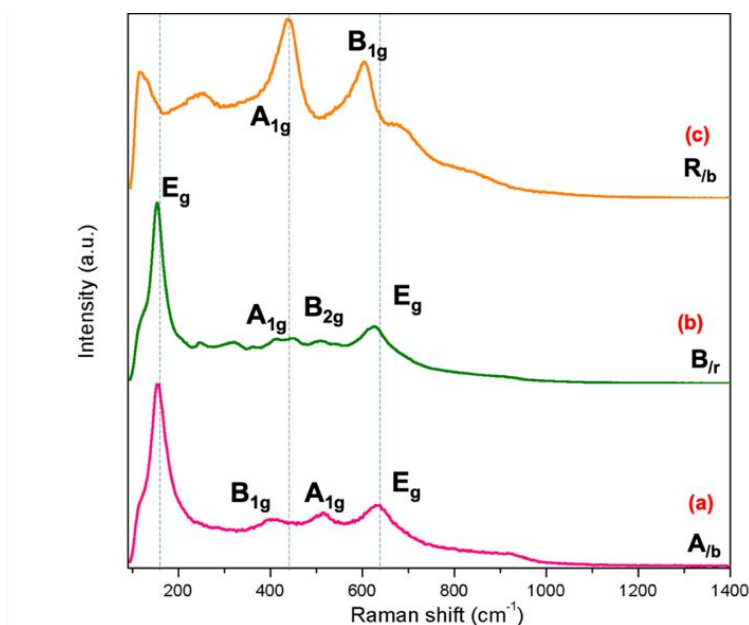


Figure S 7 Raman full spectra for the synthesized TiO₂ mixed phases; (a) anatase major, *A_b*, (b) brookite major, *B_r* and (c) rutile major, *R_b*

FTIR analysis

Figure S 8 shows the FTIR spectra for the three aqueous-synthesized mixed-phase TiO₂ NPs and P25. The wavenumber positions for the two characteristic peaks located at around 3300 cm⁻¹ (the center of the broad band) (the stretching of -OH groups) and around 1650 cm⁻¹ (the bending of adsorbed H₂O) are clearly indicated on the spectra.[2] Given that the powders have the same density, their relative -OH contents was evaluated using the mass-independent -OH % spectroscopic parameter method.[3] The quantitative spectroscopic parameter for each nanoTiO₂ sample was derived from the ratio of the integrated -OH stretching band area at around 3300 cm⁻¹ (integration between 2700 cm⁻¹ and 3700 cm⁻¹ spectral range) to the relevant SSA value for each sample. Table S 3 summarizes the obtained results. From this analysis the three synthesized nanoTiO₂ samples are seen to carry significantly higher -OH contents (14, 21 and 20 % for *A_b*, *B_r* and *R_b* respectively) than the commercial P25 at 7%.

Table S 3 % OH content derived from determination of the -OH % spectroscopic parameter

TiO ₂ products	Integrated SSA (m ² /g) Area of -OH band at 3300 cm ⁻¹ Ratio OH% Content
A_b	14
B_r	21
R_b	20
Commercial P25	7

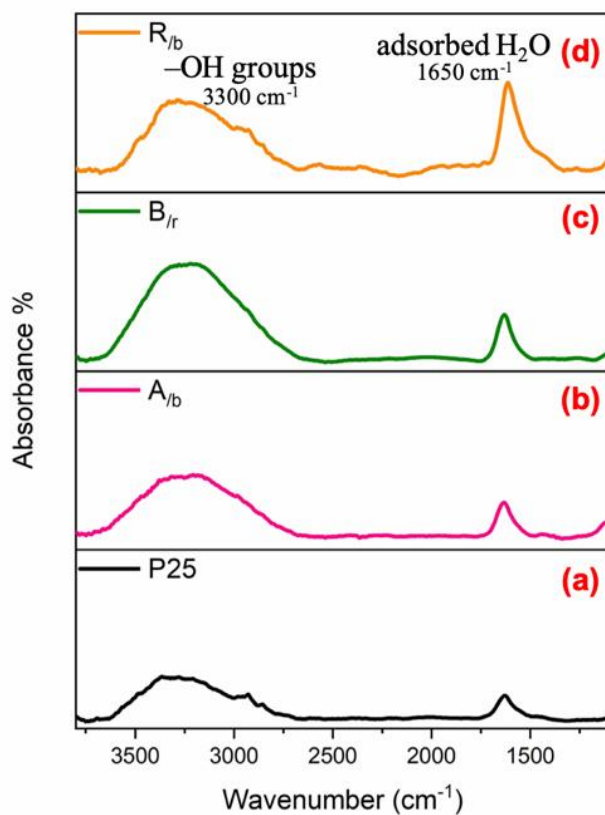


Figure S 8 FTIR spectra of aqueous-synthesized mixed-phase TiO₂ nanoparticles and P25; (a) commercial P25, (b) anatase major, A_b, (c) brookite major, B_r, and (d) rutile major, R_b

TGA analysis

Figure S 9 shows the TGA spectra for the three mixed-phase TiO₂ NPs with their weight loss compared with the commercial P25. All TiO₂ samples were heated up to 600 °C at 10 °C/minute under nitrogen gas.

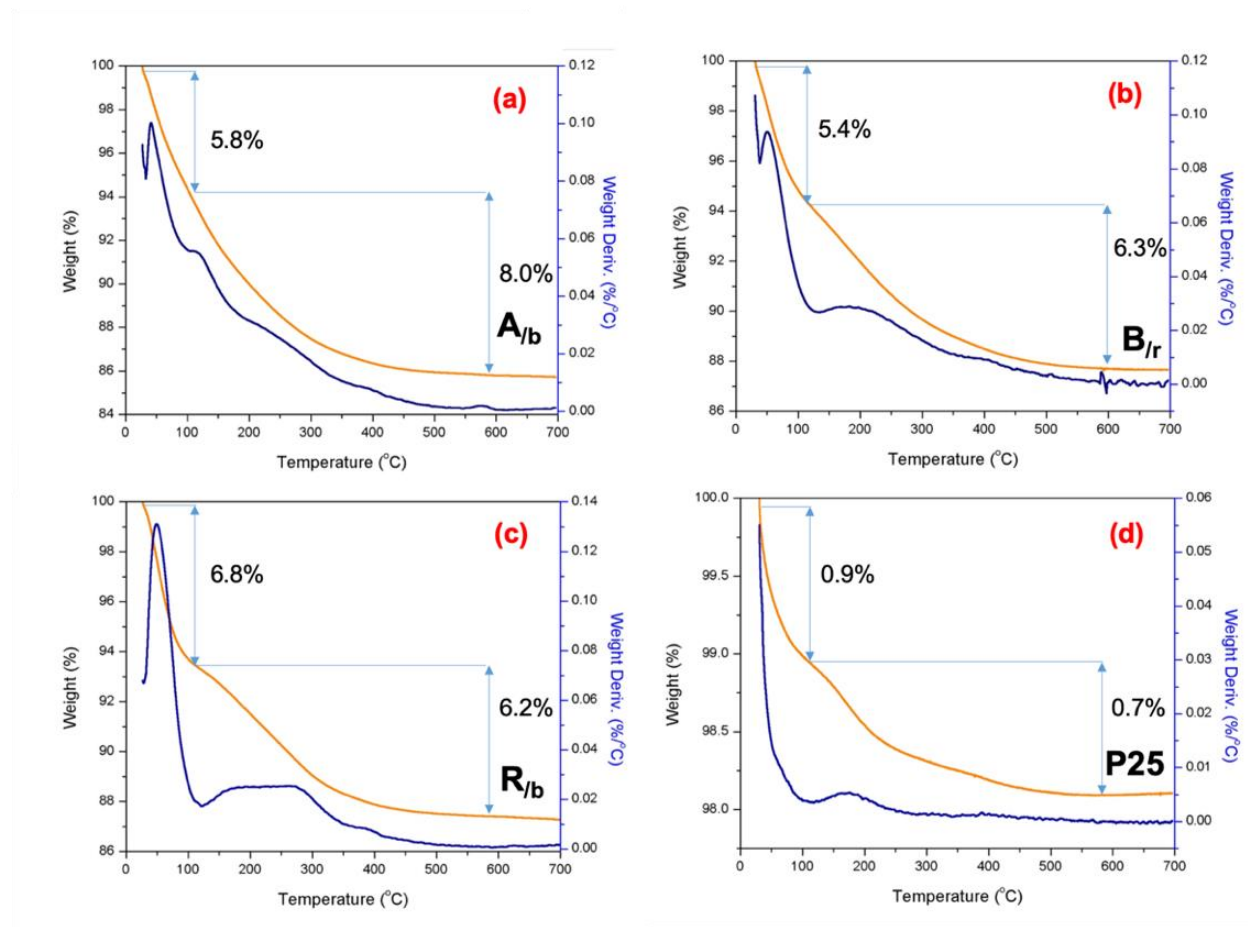
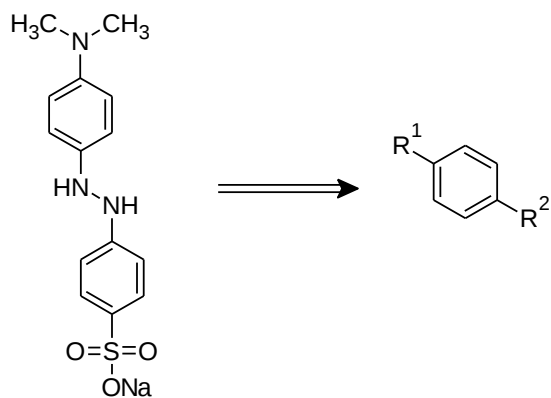


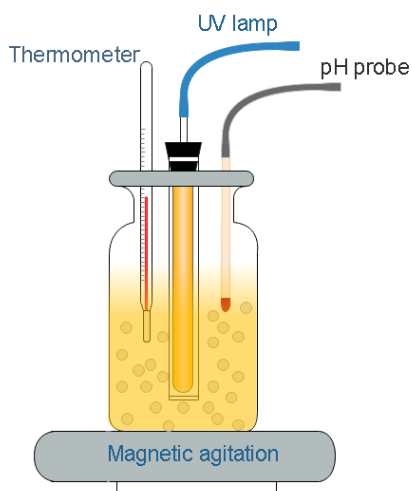
Figure S 9 TGA analysis: weight percent (orange curve) and derivative of weight percent (blue curve) of (a) anatase major, A_b , (b) brookite major, B_r , (c) rutile major, R_b , and (d) commercial P25

Photocatalytic experiments

Methyl orange (molecular structure in Schematic S 2) was used for the organic photocatalytic degradation studies and the photocatalytic reactor set up can be seen in Schematic S 3.



Schematic S 2 Simplified molecular structure of methyl orange



Schematic S 3 Schematic representation of the UV photocatalytic reactor in a box.

Methyl orange solution after the addition of the TiO_2 catalyst and after 4 h light illumination can be seen at the Figure S 10(a) and (b) respectively.

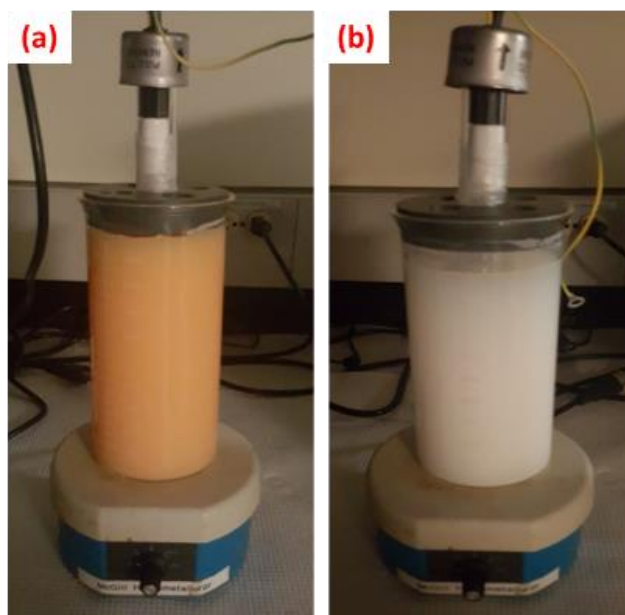


Figure S 10 Custom-made photo reactor with immersed UV light lamp used in methyl orange photo-degradation tests: (a) before light illumination; (b) after 2 h photo-illumination. UV lamp characteristics: 10 W output, wavelength range of 200-280 nm, peak at 254 nm, power density of 30 mW/cm², by Atlantic Ultraviolet Corporation

Figure S 11(a) shows UV-Vis spectra taken at specific time intervals during photo-degradation using the mixed-phase TiO₂ nanoparticles. Using a UV-Vis spectrometer we monitor the concentration of methyl orange at the characteristic peak of 464 nm.[4] Figure S 11(b) shows the Beer's Law calibration curve used to convert UV-Vis absorption data to concentration of methyl orange.

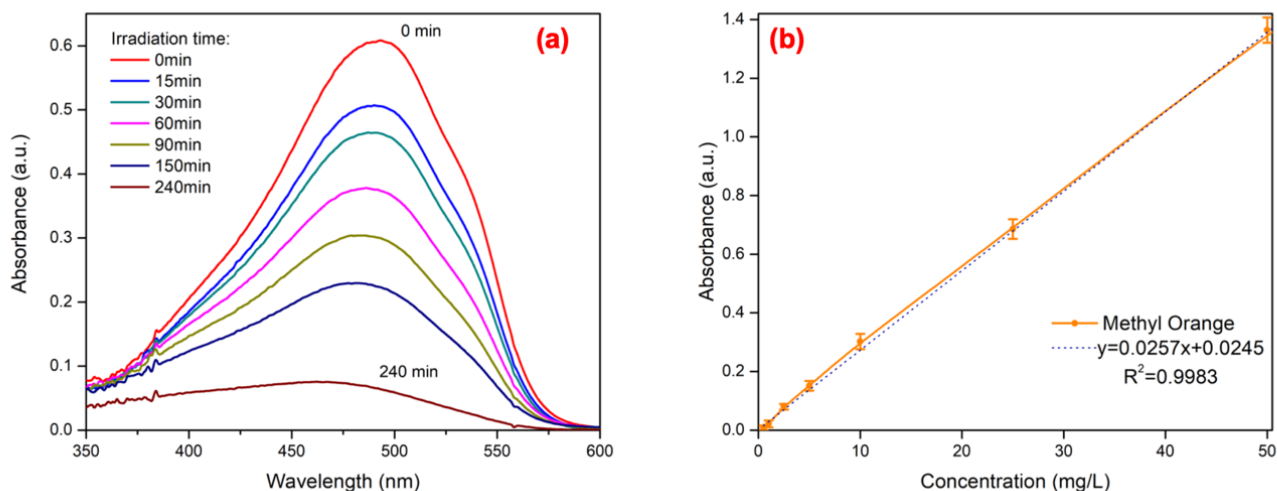


Figure S 11 (a) Example of UV-Vis spectra of methyl orange obtained at different UV illumination times to evaluate the photocatalytic degradation efficiency of one of the synthesized mixed-phase TiO₂ material (brookite major, **B_r**). Conditions; catalyst loading 1 g TiO₂/L, C_{MO}: 25 mg/L, dark equilibrium 30min and (b) Beer's law calibration curve for methyl orange

Adsorption

A typical degradation curve is shown in Figure S 12, which has two parts reflecting; (I) the adsorption of MO in the dark (30 min), followed (II) by the photo-degradation of MO under UV light illumination.

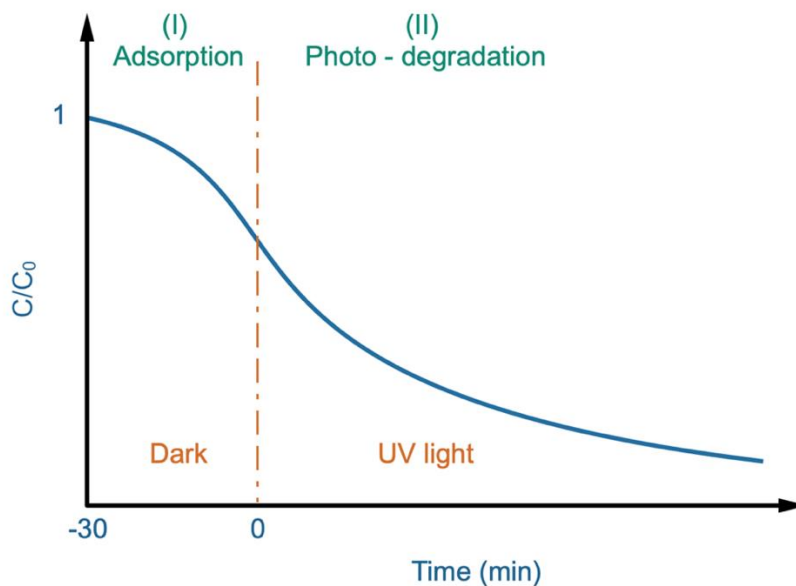


Figure S 12 Typical integrated adsorption and photo-degradation curve

Figure S 13 shows the adsorption part of the photocatalytic tests without having any light illumination for 4 h. We observe that the different TiO_2 NPs exhibit substantial variation in the adsorption percentages while also after 30 min in the dark no significant difference occurs.

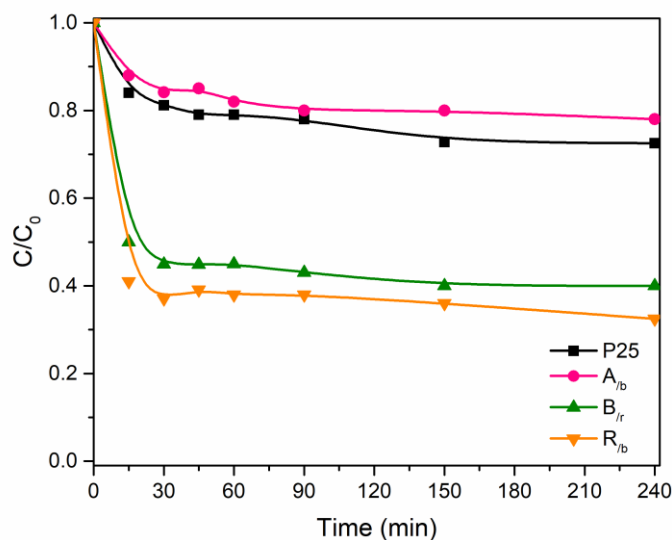


Figure S 13 Percent adsorption of MO on anatase major, A_b , brookite major, B_r , rutile major, R_b , and commercial P25 during equilibration in the dark for 4 h. Conditions; catalyst loading 1 g TiO_2/L , C_{MO} : 25 mg/L

Different pre-photocatalytic treatment processes, such as ozone treatment (Figure S 14(a)), annealing at 500 °C (Figure S 14(b)) and using the NPs without drying after synthesis (Figure S 14(c)) were evaluated. Photocatalytic tests were run with 1 g/L TiO₂ loading and 25 mg/L MO, after 30 min adsorption equilibration in the dark.

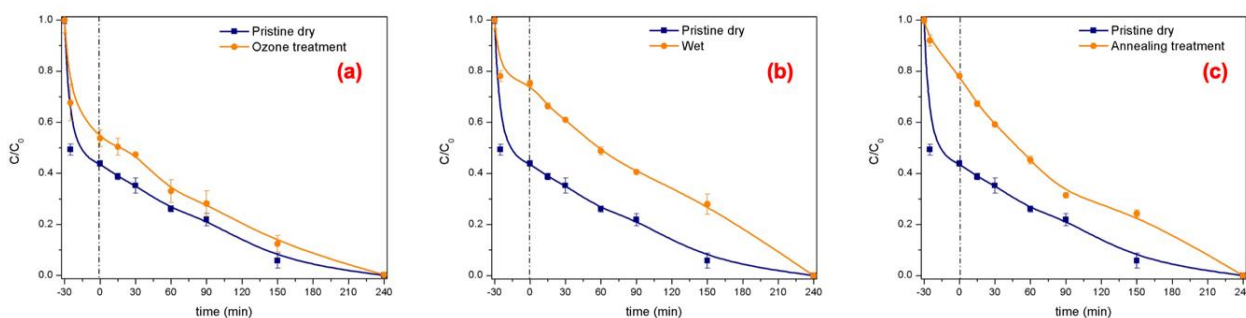


Figure S 14 Evaluation of the effect of NP pretreatment on photocatalytic degradation of methyl orange with UV light illumination; (a) ozone treatment, (b) wet before drying, (c) annealing treatment. Conditions; nanoTiO₂ used dry B_r; catalyst loading 1 g TiO₂/L, C_{MO}: 25 mg/L

The photocatalytic performance of pure-phase, mixed-phase and physical mixtures of A and B are compared in Figure S 15. The Figure clearly demonstrates that the mixed-phase nanoTiO₂ outperforms the other systems, which may be taken as indirect evidence of heterostructuring of the A and B NPs, but further work should be undertaken to provide a definitive answer.

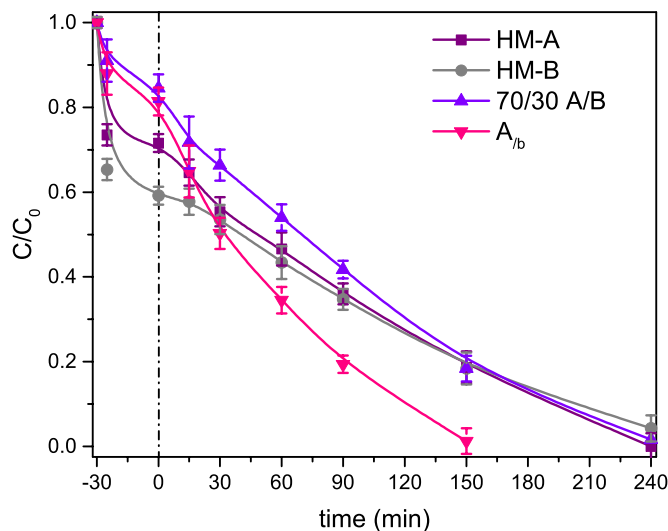


Figure S 15 Photo-assisted elimination of methyl orange with different TiO₂ nanophase particles under dark (-30 to 0 min) and UV illumination (0 to 240 min): comparison of aqueous-synthesized pure phase anatase (HM-A), brookite (HM-B), physical mixture of aqueous-synthesized pure anatase and brookite (70% A/ 30% B), and aqueous-synthesized mixed-phase (A_xB_y, 70% A/ 30% B) nanoTiO₂. Conditions; catalyst loading 1 g TiO₂/L, C_{MO}: 25 mg/L. UV lamp characteristics: 10 W output, wavelength range of 200-280 nm, peak at 254 nm, by Atlantic Ultraviolet Corporation

Kinetics

First-order kinetic analysis of the photocatalytic part of the reaction (adsorption excluded) shown in Figure S 16. The extracted photocatalytic rate constants are presented in Table S 4.

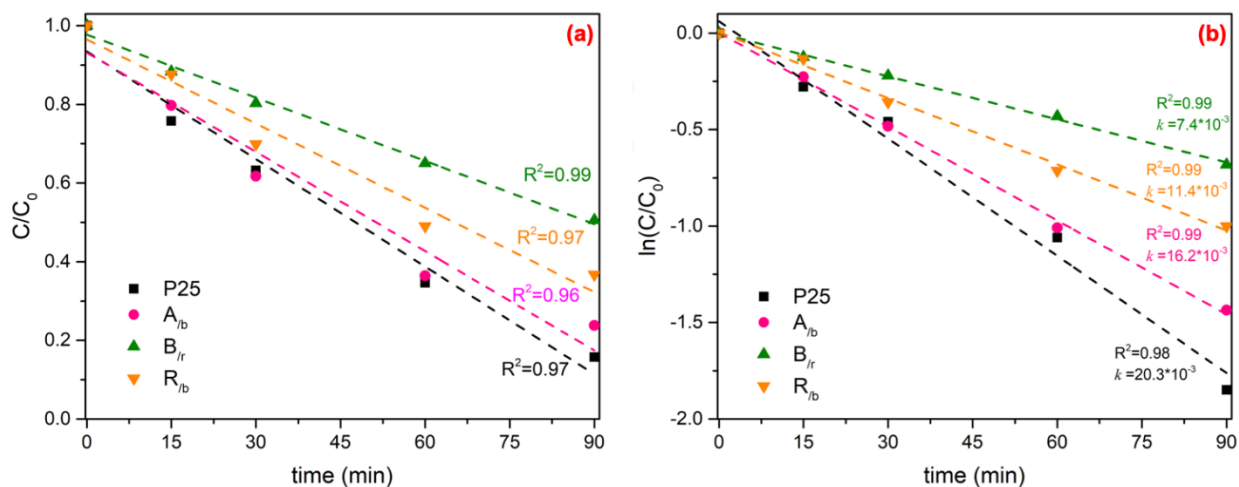


Figure S 16 Kinetic analysis of the illumination part (dark period excluded) for the different nanoTiO₂ photodegradation curves (refer to Figure 9(a)): (a) C/C_0 vs. time, and (b) $\ln(C/C_0)$ vs t

Table S 4 First-order* photocatalytic reaction rate constants of synthesized mixed-phase nanoTiO₂

TiO ₂ products	Rate constant, k (min ⁻¹)
A _{fb}	16.2 × 10 ⁻³
B _{fr}	7.4 × 10 ⁻³
R _{fb}	11.4 × 10 ⁻³
Commercial P25	20.3 × 10 ⁻³

* First-order integrated rate equation: $\ln(C/C_0) = -k t$

Reproducibility

The quality of reproducibility data during the photodegradation tests is exemplified with the C/Co vs. time curves shown in Figure S 17.

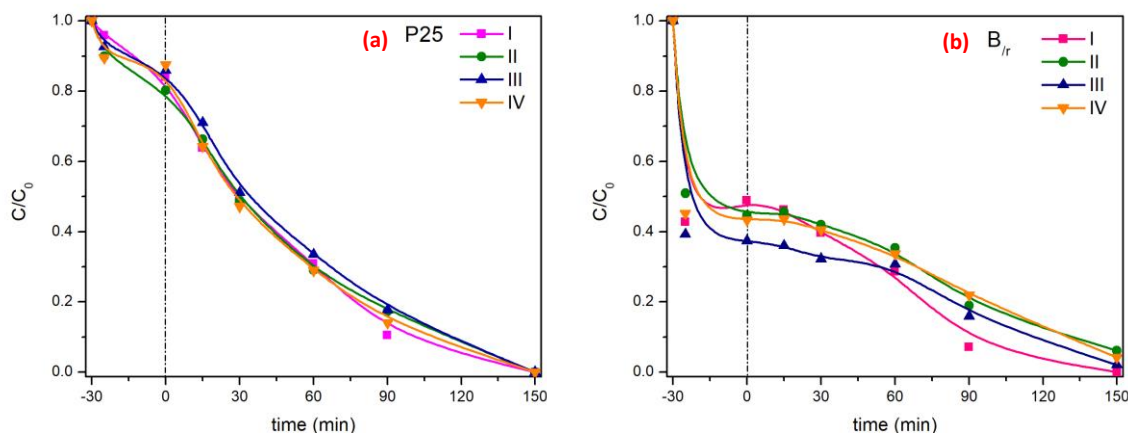


Figure S 17 Characteristic reproducibility data of photocatalytic tests for (a) commercial P25 and (b) synthesized mixed phase B_r TiO_2 . Conditions; catalyst loading 1 g TiO_2/L , C_{MO} : 25 mg/L

Band gap calculation

The UV range is related to the band gap adsorption of each TiO_2 , Figure S 18(a). Each nano TiO_2 , as a semiconductor, has a band gap energy, which can be determined by the Kubelka–Munk function, converting the reflectance measurements, R to the absorption coefficient, F(R) (Equation S 1 and Equation S 2).[5] Figure S 18(b) shows the tauc plots where the $(F(R) \cdot h\nu)^{1/2}$ is plotted versus the photon energy. The indirect band gap (E_g) is extrapolated by the linear segment of the spectrum.

$$\alpha * h\nu = A(h\nu - E_g)^n \quad \text{Equation S 1}$$

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad \text{Equation S 2}$$

Where:

- α : absorption coefficient
- $h\nu$: photon energy
- E_g : bandgap energy
- A : band tailing parameter,
- n : depends on the type

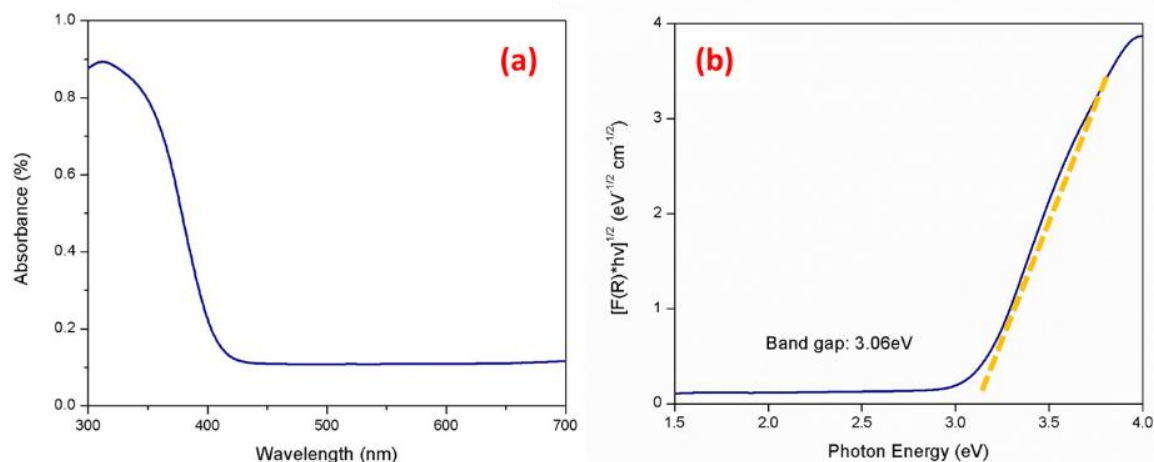


Figure S 18 Band gap calculation process, example of anatase major, A_b TiO_2 nanomaterial: (a) UV-Vis absorbance spectrum and (b) tauc plot, a linear extrapolation of the curve determines the band gap

Table S 5 Bandgap comparison of synthesized pure-phase Anatase, Brookite and Rutile TiO_2 nanoparticles with synthesized mixed-phase TiO_2 nanoparticles; A_b , B_r , R_b

Pure-phase TiO_2 Products	E_g (eV)	Ref Reyes-Coronado et al.[5]	Mixed-phase TiO_2 Products	E_g (eV)
A	3.16	3.21	A_b	3.15
B	3.1	3.13	B_r	3.01
R	3.0	3.0	R_b	2.9
Commercial P25				3.2

References

- [1] Z. Luo, A.S. Poyraz, C.H. Kuo, R. Miao, Y.T. Meng, S.Y. Chen, T. Jiang, C. Wenos, S.L. Suib, Crystalline Mixed Phase (Anatase/Rutile) Mesoporous Titanium Dioxides for Visible Light Photocatalytic Activity, *Chemistry of Materials* 27(1) (2015) 6-17.
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- [3] P.B. Coleman, *Practical sampling techniques for infrared analysis*, CRC Press, 1993.
- [4] Y. Su, Y. Yang, H. Zhang, Y. Xie, Z. Wu, Y. Jiang, N. Fukata, Y. Bando, Z.L. Wang, Enhanced photodegradation of methyl orange with TiO_2 nanoparticles using a triboelectric nanogenerator, *Nanotechnology* 24(29) (2013) 295401.
- [5] D. Reyes-Coronado, G. Rodríguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R.d. de Coss, G. Oskam, Phase-pure TiO_2 nanoparticles: anatase, brookite and rutile, *Nanotechnology* 19(14) (2008) 145605.