Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Factors impacting the aggregation/agglomeration and the photocatalytic activity of highly crystalline spheroid- and rod-shaped TiO_2 nanoparticles in aqueous solutions

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Electronic Supporting Material

1. Synthesis of TiO_2 nanoparticles

Table S1. Concentration of the main reagents and the corresponding molar concentration ratios used for the synthesis of TiO_2 nanoparticles.

Concentration of reagents (M)			Molar concentration ratios	
AA	**TTIP**	**BzOH**	**[AA] / [BzOH]**	**[BzOH] / [TTIP]**
Nano-spheres*				
-	0.96	6.86	-	7.12
-	0.67	7.69	-	11.42
-	0.56	8.00	-	14.24
Nano-rods*				
1.59	0.61	6.99	0.23	11.42
2.26	0.59	6.69	0.34	11.42
0.82	0.64	7.33	0.11	11.42
2.88	0.56	6.41	0.45	11.42
0.69	0.54	7.68	0.09	14.24
0.56	0.54	7.74	0.07	14.24
0.42	0.55	7.80	0.05	14.24
0.28	0.55	7.87	0.04	14.24
0.14	0.56	7.93	0.02	14.24
1.34	0.52	7.38	0.18	14.24
2.18	0.84	6.00	0.36	7.12
0.66	0.93	6.59	0.10	7.12
2.70	0.81	5.78	0.47	7.12

** expected shape of TiO_2 nanoparticles*

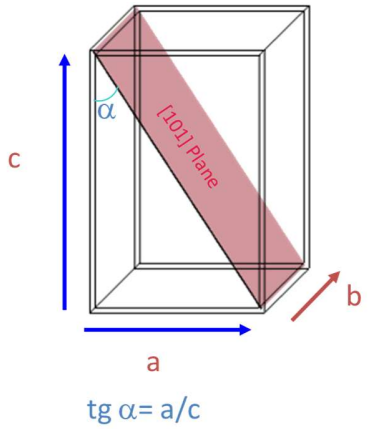

Figure S1. Schematic representation of the crystalline structure showing the [101] plane.

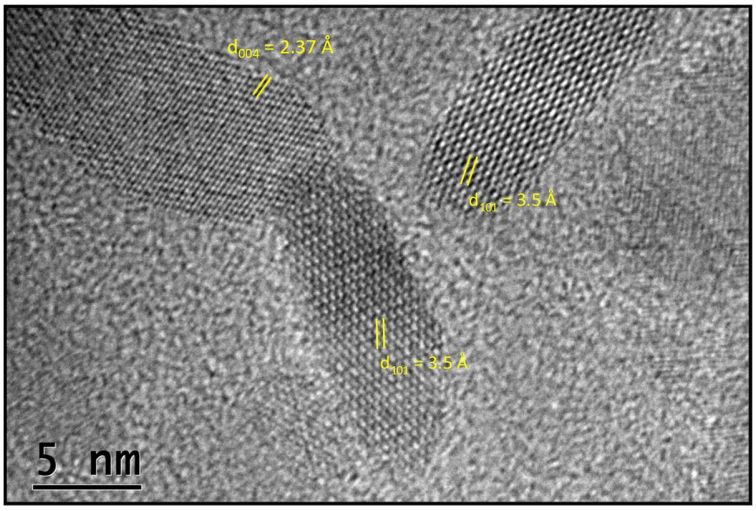

Figure S2. Additional HRTEM micrography of rod-shaped TiO2 nanoparticles. The orientation of crystallographic plans [101] and [004], identified by Inter reticular distances measurement from FFT and line profile, is consistent with a growth along the c-axis.

2. Photocatalytic activity

The rate of photocatalytic reaction, r, may be determined using the Langmuir-Hinshelwood model [1, 2]

$$r = \frac{k_r K_a C}{1 + K_a C} \approx k_r K_a C = k_{app} C$$

This equation may be simplified to pseudo-first order equation as follows:

$$Ln\left(\frac{C}{C_0}\right) = -k_{app} t$$

With C_0 the initial concentration, C the concentration at time, k_r the reaction rate constant, K_a the adsorption constant and k_{cat} the apparent first-order rate constant. The pseudo-first order rate constants, k_{cat}, were thus determined from data in Figure 8 using an exponential fitting

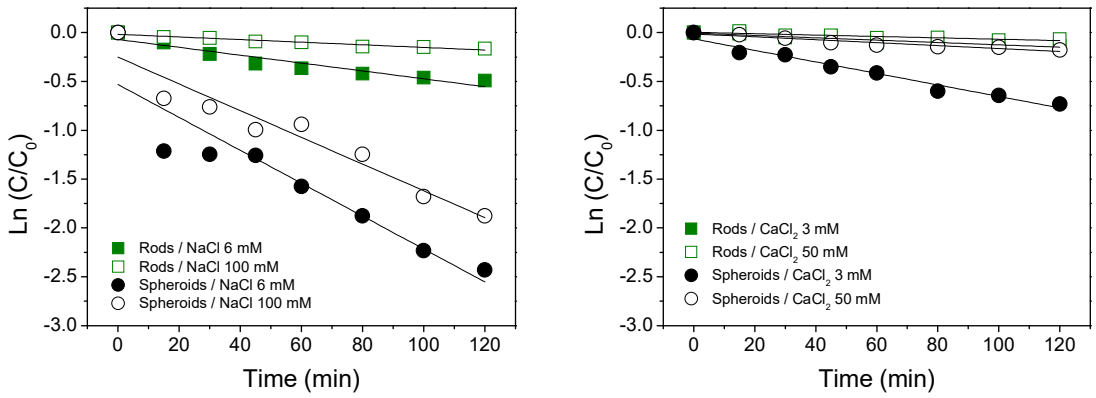

Figure S3. Photocatalytic degradation curves of methylene blue using (●,○) spheroid and (■,□) rod-shaped nanoparticles in NaCl electrolyte at concentrations of 6 (closed symbols) or 100 mM (open symbols), and in $CaCl_2$ electrolyte at concentrations of 3 (closed symbols) or 50 mM (open symbols).

Table S2. Adsorption of methylene blue on spheroid and rod-shaped TiO_2 nanoparticles in NaCl or $CaCl_2$ electrolytes after 1 h of incubation. (bdl = below detection limit).

Electrolyte / concentration (mM)		Adsorption (%)	
		Rods	Spheroids
NaCl	6	0.74	0.74
	100	1.1	3.8
$CaCl_2$	3	3.4	bdl
	50	5.1	4.8

References

1. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, *Applied Catalysis B: Environmental*, 2001, 31, 145-157.
2. K.-H. Wang, Y.-H. Hsieh, C.-H. Wu and C.-Y. Chang, *Chemosphere*, 2000, 40, 389-394.