Supporting Information

Formation Mechanism of TiO_2 Polymorphs under Hydrothermal Conditions Based on Structure Evolution of $[Ti(OH)_h(H_2O)_{6-h}]^{4-h}$ Monomers.

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Experimental

Synthesis of TiO_2

The $Ti(OH)_4$ precipitate was prepared by reaction of $TiCl_4$ and NaOH, and it was used as the precursor after centrifugal washing. The pH value of the $Ti(OH)_4$ precursor was adjusted by NaOH or HCl, and we prolonged the reaction time to dissolve $Ti(OH)_4$ and further added a certain amount of NaOH or HCl to stabilize the pH value. Then the 1.4 L suspension (0.5 mol/L Ti^{4+}) was charged into a Teflon-lined autoclave with an internal volume of 2 L. There was no initial pressure applied, and temperature of the hydrothermal synthesis was 125 °C or 150 °C with the holding time of 12 or 18 h. The obtained TiO_2 was centrifuged and washed with deionized water. After drying at 60 °C in air dry oven, the TiO_2 powder is obtained.

Phase characterization

X-ray diffraction spectra of the powders were recorded at room temperature using a powder diffractometer (Bruker D8 Advance diffractometer) employing the CuK_α radiation (λ = 1.5415 nm). The data were collected at each angle for 10 s, the interval was 0.02°, and the 2θ range was 20° to 80° for all of the samples.

Table S1. Conversion table of hydrolysis ratio under different hydrothermal conditions.

	Hydrothermal temperature (°C)	Ionic strength (mol/L)	Ion-product (pK_w)	pH value at hydrothermal temperature	pH value at room temperature (25°C)
h = 2	25	0	14.0	-	1.1
	100	0	12.3	0.2	0.2
	100	0.1	12.0	0.1	0.1
	100	1	11.9	0	0
	125	0	11.9	0	0
	125	0.1	11.6	-0.1	-0.1
	125	1	11.5	-0.2	-0.2
	150	0	11.6	-0.1	-0.1
	150	0.1	11.3	-0.3	-0.3
	150	1	11.2	-0.3	-0.3
h = 3	25	0	14.0	-	3.8
	100	0	12.3	2.9	2.9
	100	0.1	12.0	2.8	2.8
	100	1	11.9	2.7	2.7
	125	0	11.9	2.7	2.7
	125	0.1	11.6	2.6	2.6
	125	1	11.5	2.5	2.5
	150	0	11.6	2.6	2.6
	150	0.1	11.3	2.4	2.4
	150	1	11.2	2.4	2.4
h = 5	25	0	14.0	-	10.4
	100	0	12.3	9.5	11.2
	100	0.1	12.0	9.4	11.4
	100	1	11.9	9.3	11.4
	125	0	11.9	9.3	11.4

	125	0.1	11.6	9.2	11.6
	125	1	11.5	9.1	11.6
	150	0	11.6	9.2	11.6
	150	0.1	11.3	9	11.7
	150	1	11.2	9	11.8