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Supporting information for article:

In situ high-temperature X-ray diffraction study of Sc-doped titanium oxide nanocrystallites

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Part I. Detailed results of XRD Rietveld analysis and DFA

Detailed results are given in Tables S1-S4 (Rietveld) and Table S5 (DFA). Fig. S1 and Fig. S2 show lattice parameters of anatase and rutile, respectively, compared with results from the literature.

Table S1: Rietveld refinement (GSAS-II) detailed results: lattice parameters and weighted reliability factor (wR). Standard uncertainties (e.s.d.'s) are given in parentheses, while F means fixed (i.e., not refined).

T [°C]	Anatase		Rutile		Sc ₂ TiO ₅			Pt	wR [%]
	a	c	a	c	a	b	c	a	
25	3.8009(11)	9.5254(38)						3.9302(3)	3.60
100	3.8023(11)	9.5073(37)						3.9321(3)	3.58
200	3.8029(11)	9.5089(36)						3.9346(3)	3.44
300	3.7993(11)	9.5263(40)						3.9374(2)	3.40
400	3.7948(9)	9.5439(38)						3.9385(2)	3.30
500	3.7990(7)	9.5560(28)						3.9432(2)	3.23
550	3.7978(6)	9.5599(24)						3.9448(2)	3.37
575	3.7992(5)	9.5678(21)						3.9463(2)	3.36
600	3.7982(5)	9.5669(19)						3.9473(2)	3.37
625	3.7982(5)	9.5696(18)						3.9482(2)	3.34
650	3.7985(4)	9.5695(17)						3.9494(2)	3.40
675	3.7979(4)	9.5755(15)						3.9502(1)	3.40
700	3.7963(3)	9.5782(14)						3.9506(1)	3.46
725	3.7971(3)	9.5814(13)						3.9521(1)	3.58
750	3.7980(3)	9.5857(11)						3.9533(2)	3.64
775	3.7990(3)	9.5908(10)						3.9546(1)	3.50
800	3.8002(3)	9.5934(9)						3.9560(1)	3.62
825	3.8013(2)	9.5970(8)						3.9574(2)	3.76
850	3.7989(2)	9.5966(7)						3.9571(1)	3.97
875	3.8003(2)	9.5999(6)						3.9585(1)	4.10
900	3.8016(2)	9.6052(5)	4.6254(35)	2.9858(26)				3.9600(1)	4.17
925	3.8026(2)	9.6098(5)	4.6285(10)	2.9874(8)				3.9615(1)	4.48
950	3.8032(2)	9.6136(5)	4.6298(4)	2.9889(3)				3.9627(1)	4.66
975	3.8029(2)	9.6156(6)	4.6306(2)	2.9897(2)	3.846(F)	10.345(F)	10.320(F)	3.9637(1)	4.74
1000	3.8023(2)	9.6185(6)	4.6316(1)	2.9907(1)	3.853(3)	10.232(14)	10.382(14)	3.9645(1)	4.32
1025	3.8056(2)	9.6214(8)	4.6327(1)	2.9915(1)	3.856(2)	10.236(10)	10.397(9)	3.9656(1)	3.87
1050	3.8051(97)	9.6256(17)	4.6340(1)	2.9924(1)	3.858(1)	10.215(8)	10.400(7)	3.9668(1)	3.90
1075	3.8044(4)	9.6316(36)	4.6352(1)	2.9936(1)	3.865(1)	10.198(8)	10.396(5)	3.9681(1)	3.87
1100	3.8035(11)	9.6445(93)	4.6365(1)	2.9946(1)	3.864(1)	10.216(9)	10.390(5)	3.9693(1)	4.02
1125	3.7998(21)	9.6482(251)	4.6379(1)	2.9958(1)	3.865(1)	10.208(6)	10.400(4)	3.9706(1)	3.95
1150	3.8064(43)	9.6276(407)	4.6393(1)	2.9967(1)	3.866(1)	10.214(7)	10.400(5)	3.9718(1)	3.98
1175	3.8044(F)	9.6400(F)	4.6407(1)	2.9979(1)	3.866(1)	10.221(7)	10.399(4)	3.9730(1)	3.92
1200			4.6424(1)	2.9989(1)	3.869(1)	10.196(9)	10.411(5)	3.9740(1)	4.28

Table S2: Rietveld refinement (GSAS-II) detailed results: crystallites size [nm]. Standard uncertainties are given in parentheses, while F means fixed (i.e., not refined).

T [°C]	Anatase			Rutile	Sc ₂ TiO ₅
	equatorial	axial	D _{eq}	Diameter	Diameter
25	4.7(2)	6.9(6)	5.4(3)		
100	4.7(1)	6.7(2)	5.3(1)		
200	4.6(2)	6.9(6)	5.2(3)		
300	4.7(2)	6.5(6)	5.2(3)		
400	5.0(2)	7.1(6)	5.6(3)		
500	5.5(2)	7.2(4)	6.0(3)		
550	6.2(2)	8.0(4)	6.7(3)		
575	7.0(2)	8.8(4)	7.5(3)		
600	7.5(1)	9.9(2)	8.3(1)		
625	7.8(1)	9.5(2)	8.3(1)		
650	8.4(2)	10.2(4)	8.9(3)		
675	9.4(1)	11.4(2)	10.0(1)		
700	10.3(2)	13.2(6)	11.2(3)		
725	10.9(1)	13.6(3)	11.7(2)		
750	12.1(1)	15.6(3)	13.2(2)		
775	13.4(3)	16.8(6)	14.4(4)		
800	14.9(1)	18.2(3)	15.9(2)		
825	17.3(3)	21.7(8)	18.7(4)		
850	19.5(4)	26.1(1.1)	21.5(6)		
875	22.6(5)	29.9(1.2)	24.8(7)		
900	27.5(2)	38.3(8)	30.7(4)	75(20)	
925	34.9(3)	48.8(1.3)	39.0(6)	123(15)	
950	44.1(5)	61.4(2.2)	49.2(1.0)	187(14)	
975	51.6(7)	68.7(3.1)	56.7(1.4)	227(10)	52(25)
1000	60.5(3.1)	83.0(9.1)	67.2(4.7)	220(15)	42(10)
1025	77.1(1.8)	94.0(7.3)	82.4(3.4)	237(14)	51(7)
1050	89.4(4.2)	98.0(19.6)	92.2(8.9)	285(18)	58(7)
1075	88.0(7.8)	106.9(5.3)	93.9(7.1)	290(18)	81(11)
1100	80.0(16.6)	66.8(39.8)	75.3(24.5)	286(18)	102(16)
1125	77(F)	62(F)	71.6(0)	315(21)	126(20)
1150	80(F)	68(F)	75.8(0)	322(22)	125(21)
1175	90(F)	60(F)	78.6(0)	314(7)	179(9)
1200				359(30)	209(52)

Table S3: Rietveld refinement (GSAS-II) detailed results: wt.% of the phases

T [°C]	anatase	rutile	Sc ₂ TiO ₅
25	100	0	0
100	100	0	0
200	100	0	0
300	100	0	0
400	100	0	0
500	100	0	0
550	100	0	0
575	100	0	0
600	100	0	0
625	100	0	0
650	100	0	0
675	100	0	0
700	100	0	0
725	100	0	0
750	100	0	0
775	100	0	0
800	100	0	0
825	100	0	0
850	100	0	0
875	100	0	0
900	97.2(1.1)	2.8(7)	0
925	93.1(1.3)	6.9(7)	0
950	84.3(1.0)	15.7(7)	0
975	69.6(6)	28.7(8)	1.7(5)
1000	54.3(6)	42.4(3)	3.3(4)
1025	34.6(4)	57.5(2)	7.8(1.0)
1050	19.8(4)	74.0(2)	6.1(6)
1075	8.5(3)	85.7(2)	5.8(5)
1100	4.0(4)	90.2(2)	5.8(5)
1125	1.7(2)	92.1(1)	6.3(5)
1150	1.1(2)	92.5(1)	6.4(6)
1175	0.3(1)	92.2(1.5)	7.5(9)
1200	0	91.6(1)	8.4(5)

Table S4: Rietveld refinement (GSAS-II) results: Ti s.o.f. and U_{iso} of Ti and O.

T [°C]	Anatase			Rutile	
	Ti s.o.f.	Ti U _{iso}	O U _{iso}	Ti s.o.f.	Ti U _{iso} / O U _{iso} ***
25	0.80(3)	0.006(5)	0.019(6)		
100	0.77(3)	0.008(5)	0.017(6)		
200	0.78(3)	0.006(7)	0.020(7)		
300	0.86(4)	0.005(7)	0.021(7)		
400	0.91(5)	0.007(6)	0.021(7)		
500	0.93(3)	0.005(5)	0.014(5)		
550	0.92(2)	0.006(4)	0.020(4)		
575	0.92(1)	0.007(3)	0.022(4)		
600	0.97(2)	0.007(3)	0.018(4)		
625	0.89(1)	0.012(2)	0.019(4)		
650	0.93(1)	0.014(3)	0.019(3)		
675	0.92(1)	0.012(3)	0.023(3)		
700	0.96(2)	0.011(3)	0.016(3)		
725	0.96(1)	0.011(2)	0.021(3)		
750	0.99(1)	0.012(2)	0.011(3)		
775	0.98(1)	0.012(2)	0.014(3)		
800	0.99(1)	0.016(1)	0.016(1)		
825	1.00(0)	0.013(1)	0.002(3)		
850	1.00(1)	0.014(2)	0.009(3)		
875	1.00(2)	0.013(2)	0.014(0)		
900	1.00(0)	0.013(1)	0.011(3)	0.721(88)*	0.000(F)
925	1.00(1)	0.016(1)	0.016(3)	0.817(42)	0.002(F)
950	1.00	0.022(2)	0.019(4)	0.839(20)	0.002(F)
975	1.00	0.036(2)	0.030(5)	0.876(12)	0.002(F)
1000	1.00	0.053(3)	0.050(6)	0.939(6)	0.000(F)
1025	1.00	0.067(4)	0.061(9)	0.949(5)	0.001(1)
1050	1.00	0.079(9)	0.081(18)	0.965(4)	0.007(1)
1075	1.00	0.071(20)	0.052(35)	0.965(4)	0.013(1)
1100	1.00	0.063(35)	0.070(85)	0.978(4)	0.013(1)
1125	1.00	0.031(34)**	0.031(34)**	0.962(4)	0.015(1)
1150	1.00	0.044(69)**	0.044(69)**	0.966(4)	0.014(1)
1175	1.00	0.042(F)	0.040(F)	0.936(6)	0.019(1)
1200				1.002(5)	0.011(1)

F=Fixed

* too small amount for accurate Ti s.o.f. evaluation.

** U_{iso} of Ti and O were constrained to be the same.

Table S5: DFA (DEBUSSY 2.2) detailed results: anatase NC size distribution, Ti s.o.f, U_{iso} of Ti and O, weighted reliability factor (wR) and goodness of fit (GoF).

T [°C]	D _{a,b}	L _c	uni. diameter [nm]	Ti_O ₁ [*]	Ti_O ₀ [*]	Ti_O _L [*]	Ti U _{iso}	O U _{iso}	STR_i**	wR [%]	GoF
25	4.3±1.5	4.9±2.3	4.7±1.6	0.626	-	-	0.025	0.014		3.3	1.3
100	4.5±1.7	5.1±2.4	4.9±1.7	0.695	-	-	0.010	0.035		3.4	1.4
200	4.2±1.5	5.5±2.5	4.8±1.8	0.745	-	-	0.008	0.038		3.2	1.4
300	4.4±1.5	4.8±2.4	4.7±1.8	0.774	-	-	0.013	0.030		3.2	1.3
400	4.6±1.6	4.9±2.4	5.0±2.0	0.769	-	-	0.016	0.038		3.1	1.2
500	5.0±1.7	5.1±2.5	5.4±2.1	0.813	-	-	0.010	0.032		3.0	1.2
550	5.8±1.8	5.9±2.6	6.3±2.3	0.831	-	-	0.008	0.033		3.0	1.2
575	6.2±1.9	6.0±2.4	6.7±2.3	0.846	-	-	0.010	0.036		3.0	1.2
600	6.5±2.2	6.7±3.1	7.2±2.8	0.902	-	-	0.011	0.029		3.0	1.2
650	7.2±2.3	7.4±3.9	8.0±3.1	0.877	-	-	0.012	0.035		2.9	1.2
700	8.7±2.7	8.2±3.7	9.1±3.3	0.885	-	-	0.013	0.034		3.0	1.2
750	9.8±3.0	10.6±5.1	11.1±4.2	0.946	0.918	16.491	0.014	0.025	1.002	3.0	1.2
800	12.0±4.3	12.9±5.3	13.5±4.6	1.000	0.966	24.700	0.016	0.019	1.001	3.1	1.2
850	15.3±5.6	16.3±7.8	17.2±6.2	1.000	0.787	5.434	0.016	0.014	1.002	3.5	1.4
900	21.4±8.3	23.9±10.9	24.0±7.2	1.000	0.987	1.072	0.020	0.016	1.002	4.1	1.6

* 25-700°C range: parameter Ti_O1 describes the Ti s.o.f. independent of size.

750-900°C range: Parameter Ti_O1 describes the Ti s.o.f. of the largest size, Ti_O0 describes the s.o.f. factor at the smallest size and Ti_OL describes the growth/decay constant of the s.o.f.

** STR_i represents lattice expansion

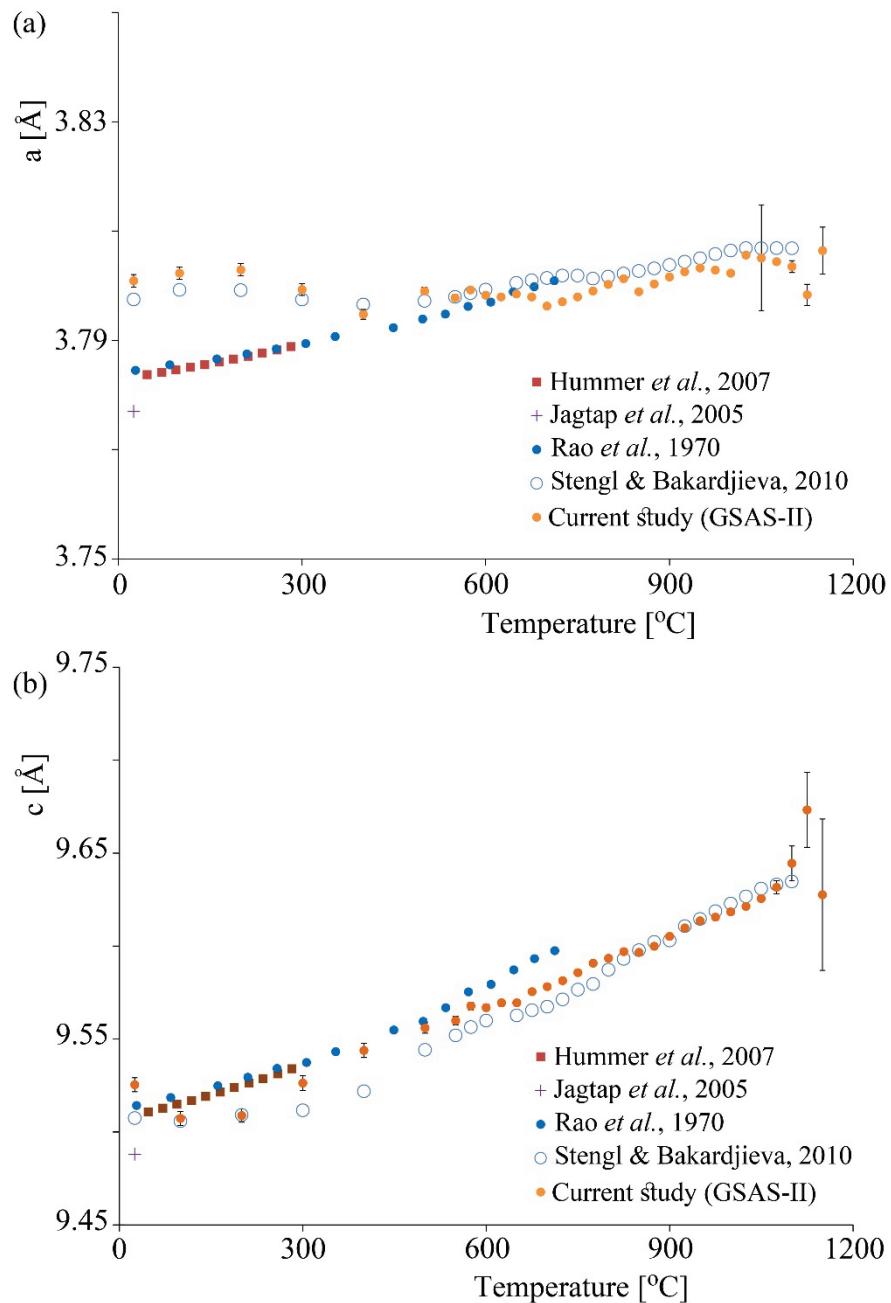


Fig. S1: Anatase lattice parameters (GSAS-II) as function of temperature compared with other *in-situ* XRD results reported in the literature for pure anatase (Hummer *et al.*, 2007; Jagtap *et al.*, 2005; Rao *et al.*, 1970) and Mo-doped anatase (Stengl & Bakardjieva, 2010). The standard uncertainties are quite large at high temperatures, especially from 1125 °C, as the amount of anatase decreases to a few percent or less.

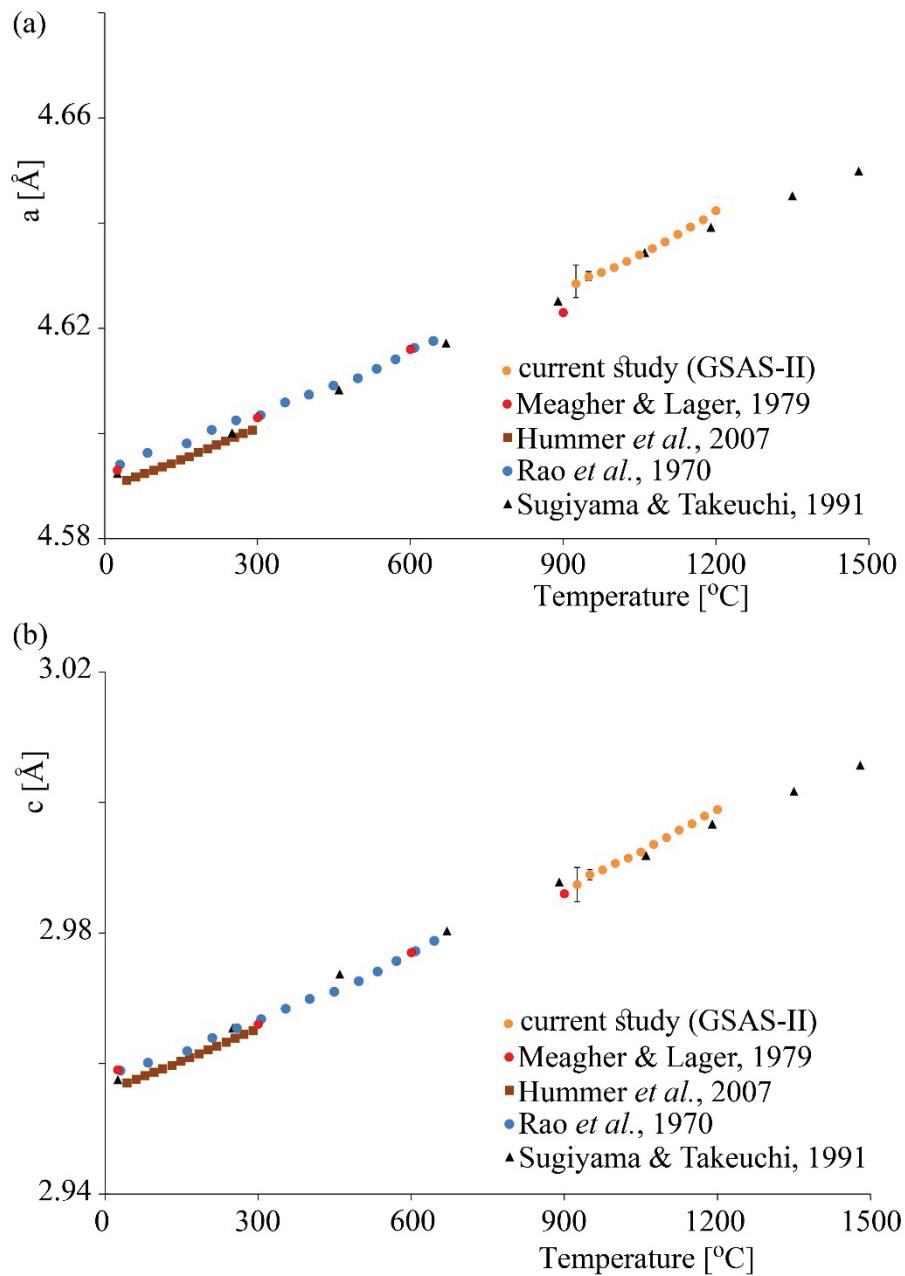


Fig. S2: Rutile lattice parameters (GSAS-II) as function of temperature. Additional results from other *in-situ* experiments are also shown (Rao *et al.*, 1970; Meagher & Lager, 1979; Sugiyama & Takeuchi, 1991; Hummer *et al.*, 2007).

Part II. Lattice parameters of Pt.

The lattice parameters of Pt as a function of temperature are given in Fig. S3, along with results from the literature. The measured lattice parameters fit well with the literature except for the range of 25-200 °C, where there is a slight difference in the lattice parameters of 0.005-0.006 Å (at higher temperatures, 300-1200 °C, there is ~0.0017 Å difference on average).

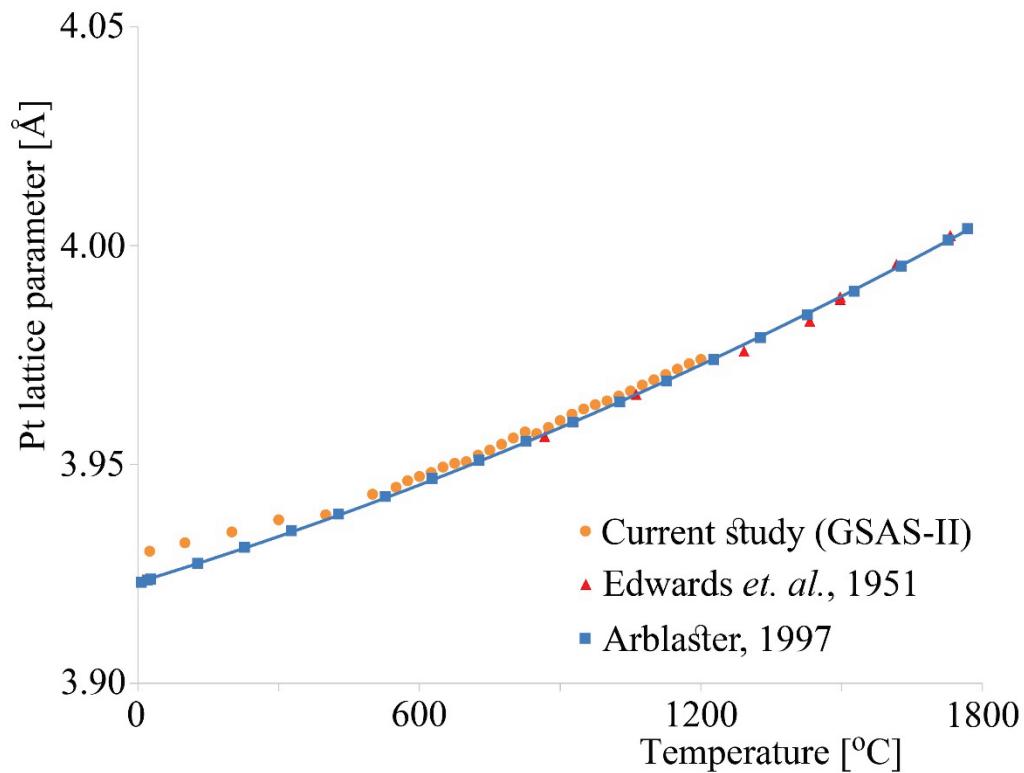


Fig. S3: The lattice parameter of Pt as a function of temperature compared with the literature (Edwards *et al.*, 1951; Arblaster, 1997).

Part III. HRTEM and SAED analyses

High-resolution transmission electron microscopy (HRTEM) was also used for observing the particle size distribution (PSD) and analysis of the crystal structure of 4SDT bulk sample annealed from 25 to 950 °C. Fig. S4 (a-f) represent the size distribution histograms obtained by HRTEM. The size distributions obtained by HRTEM for 4SDT sample at 25 °C and annealed at 200-600 °C (Fig. S4 (a-d)) could be approximated to a log-normal distribution. As the annealing temperature increases, the average values of the size (Table 1 in the manuscript) and also the dispersion of sizes increases.

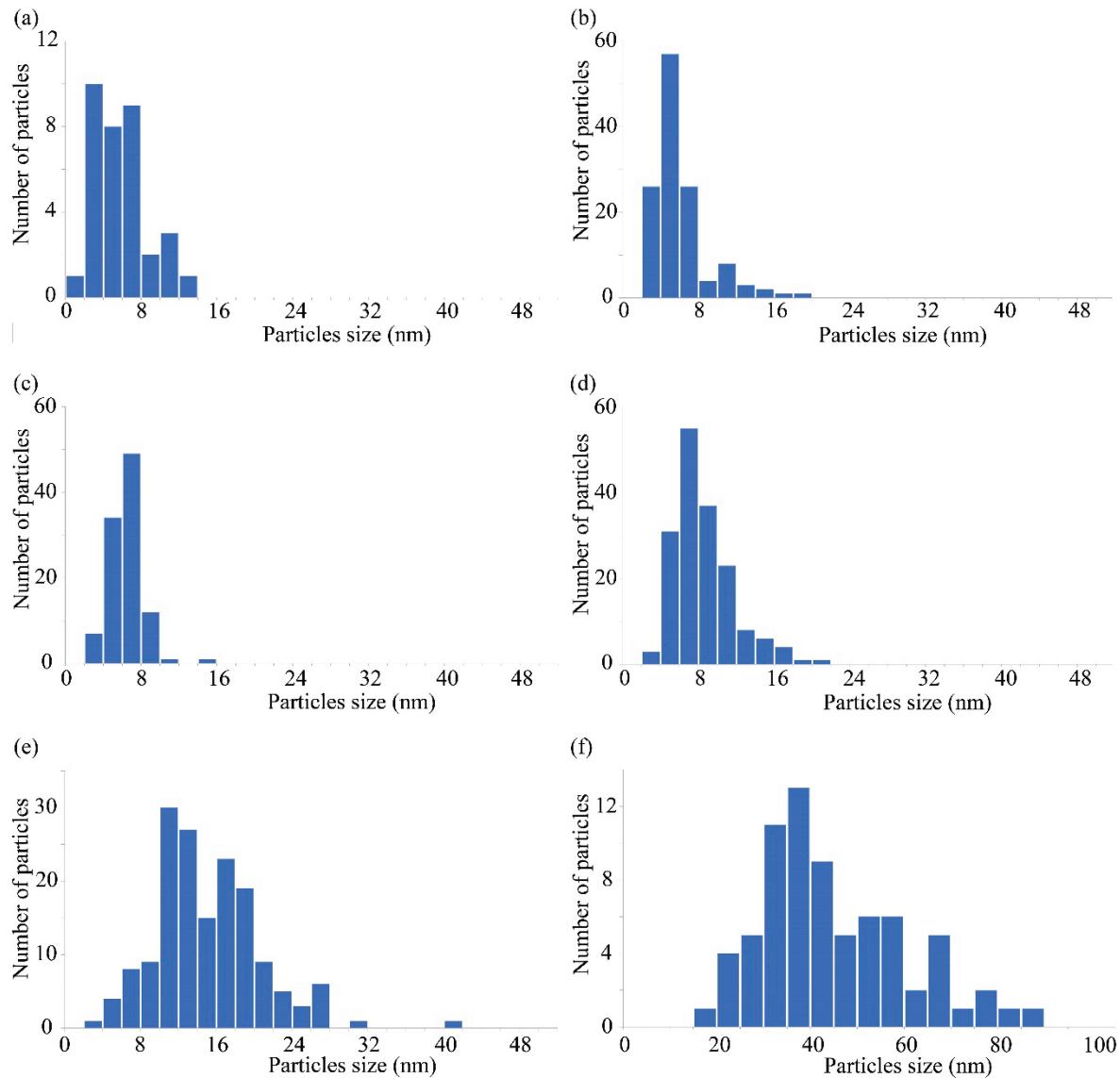


Fig. S4: Histograms of particle size distribution obtained from HRTEM images (a) 4SDT sample at 25 °C, (b-f) 4SDT annealed at 200, 400, 600, 800 and 950 °C.

Fig. S5 shows the SAED pattern of the 4SDT samples as a function of annealing temperature, together with the corresponding calculated intensities for each ring radii. The SAED patterns of sample 4SDT obtained at 25 °C and annealed 4SDT from 200 to 800 °C resemble the concentric ring patterns produced by anatase NCs with random orientations (Fig. S5 (a)-(e)). The extracted d -spacings from these patterns (insets in Fig. S5a-e) were 3.52, 2.43, 2.38, 2.33, 1.89 and 1.70 Å corresponding to (101), (103), (004), (112), (200) and (105)/121 atomic planes of anatase phase (ICDD PDF 21-1272; shown on the left hand side of Fig. S5 (a)-(e)). Several few reflections, appearing for sample 4SDT annealed at 950 °C, have been identified to be 3.24, 2.48 and 2.05 Å (see inset in Fig. S5f), corresponding to (110), (101) and (210) atomic planes of the rutile phase (ICDD PDF 21-1276).

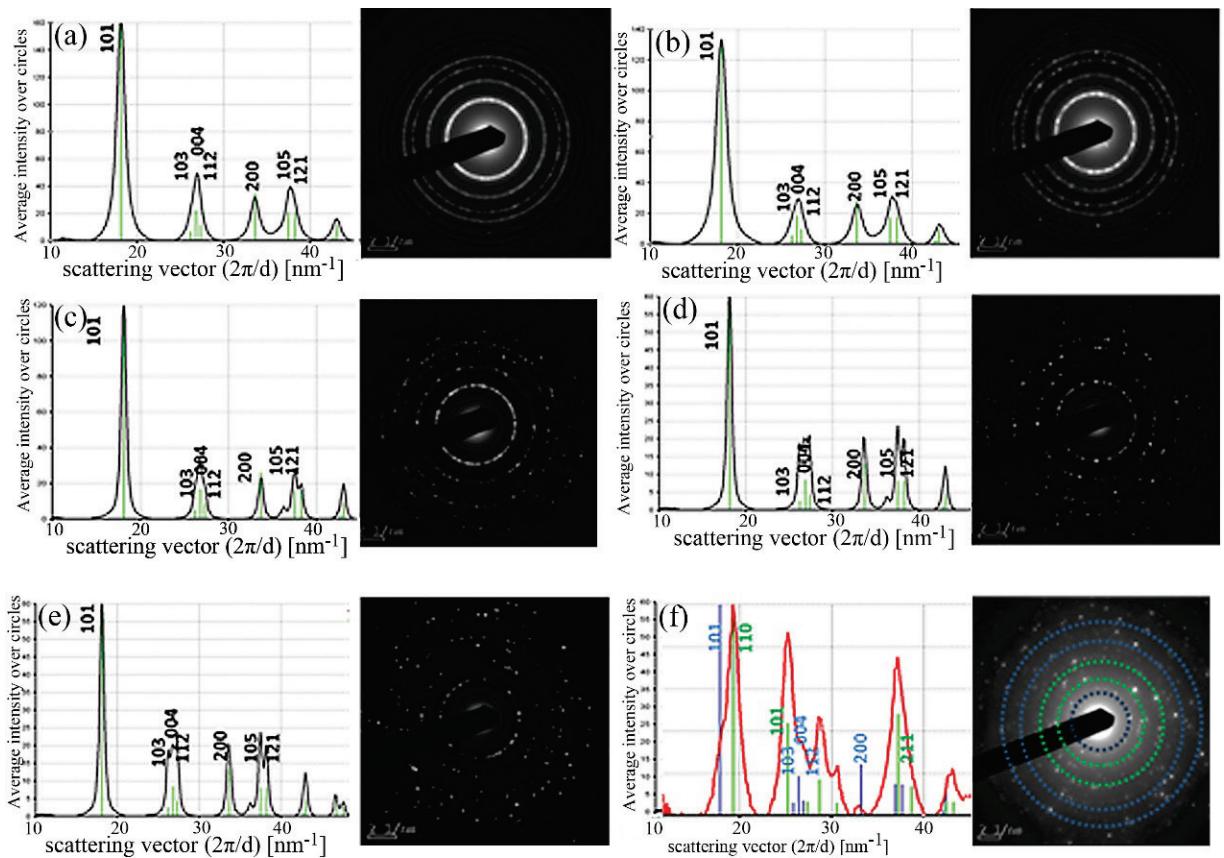


Fig. S5: SAED patterns together with the extracted intensities (a) 4SDT sample at 25 °C, (b-f) 4SDT annealed at 200, 400, 600, 800 and 950 °C. The vertical lines mark XRD intensities for interatomic planes obtained from ICDD PDF 21-1272 (anatase; green (a-e), blue (f)) and ICDD PDF 21-1276 (rutile; green (f)).

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