Supporting information

Non-classical growth of brookite nanorods

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1. XRD analysis of the samples.

XRD patterns were registered using the external standards (corundum and silicon). To avoid microabsorption and "rock-in-the-dust" effects, corundum and silicon were used with slightly larger brookite crystallite sizes (about 200-500 nm). The determination of the phase composition was performed using the ICDD PDF-2 database. The le Bail [1] method of full profile analysis was used for determination of integral intensities. In Fig. S1, XRD patterns of the single-phase brookite SP-180-48 sample obtained using different internal standards (corundum and silicon) are shown. Differential curves illustrate the quality of full-profile analysis. All XRD patterns analyzed in the paper had a goodness of fit (GOF) of no more than 2.0, with profile and weighted R-factors less than 7.0 and 8.0, respectively. XRD profiles were fitted using JANA2006 software [2]. Raw XRD patterns of all the samples are presented in Fig. S2. Crystallite sizes and phase composition of all the samples are summarized in Table S1.

Corundum was used for the quantitative determination of the phase composition of all samples (including the content of the amorphous phase) as an external standard, taking into account the amorphous phase. The fraction of crystalline phases was determined using the integral intensities of the reflections $I(A_i)$ and Reference Intensity Ratios RIR_i (1) [3].

$$\omega_{XRD}(A_i) = \frac{\overline{I(A_i)}}{\overline{RIR_i}} \Big/ \sum \frac{\overline{I(A_i)}}{\overline{RIR_i}} \qquad (1)$$

The fraction of the external crystalline standard measured by XRD differed from the real one due to the presence of amorphous phase in the sample ((2) and (3)).

$$\omega_{real}(Al_2O_3) = \frac{m(Al_2O_3)}{m(Al_2O_3) + m(Sample)} \qquad (2)$$

$$\omega_{XRD}(Al_2O_3) = \frac{m(Al_2O_3)}{m(Al_2O_3) + \sum m(Crystalline\ phases)} \qquad (3)$$

The fraction of the amorphous phase was calculated by the following equation (4).

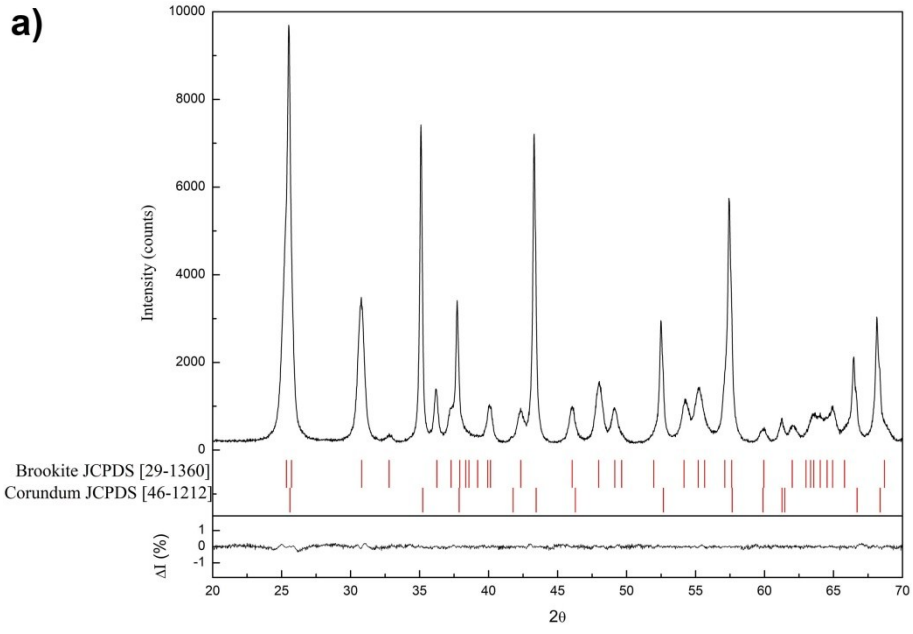
$$\omega(amorphous\ phase) = \frac{\frac{m(Al_2O_3)}{\omega_{XRD}(Al_2O_3)} - m(Sample) - m(Al_2O_3)}{m(Al_2O_3) + m(Sample)} \qquad (4)$$

The average size of the crystallites, which corresponds to crystallite size, was calculated using modified Scherrer equations ((5) and (6)).

$$p_{\perp} = \frac{180K\lambda}{\pi X} \qquad (5)$$

$$p_{||} = \frac{180K\lambda}{\pi(X + X_a)} \qquad (6)$$

Here, K is a parameter depending on the shape of the particles (K=0.9), λ is the X-ray wavelength, X, X_a are the parameters of refining the X-ray peak profile (in the case of isotropic particles, X_a was 0).



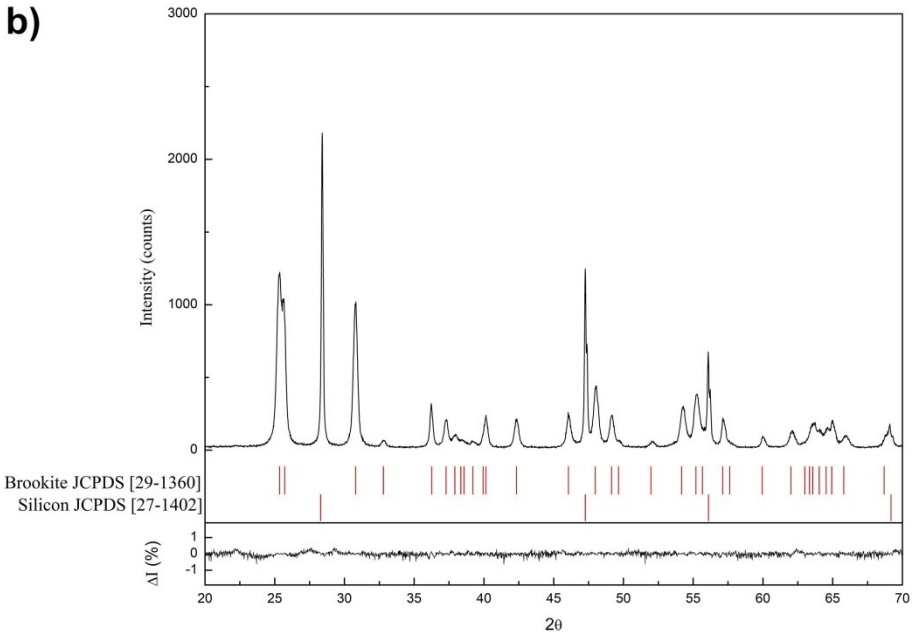


Fig. S1. XRD patterns of the single-phase brookite SP-180-48 sample registered using different internal standards: corundum (a) and silicon (b).

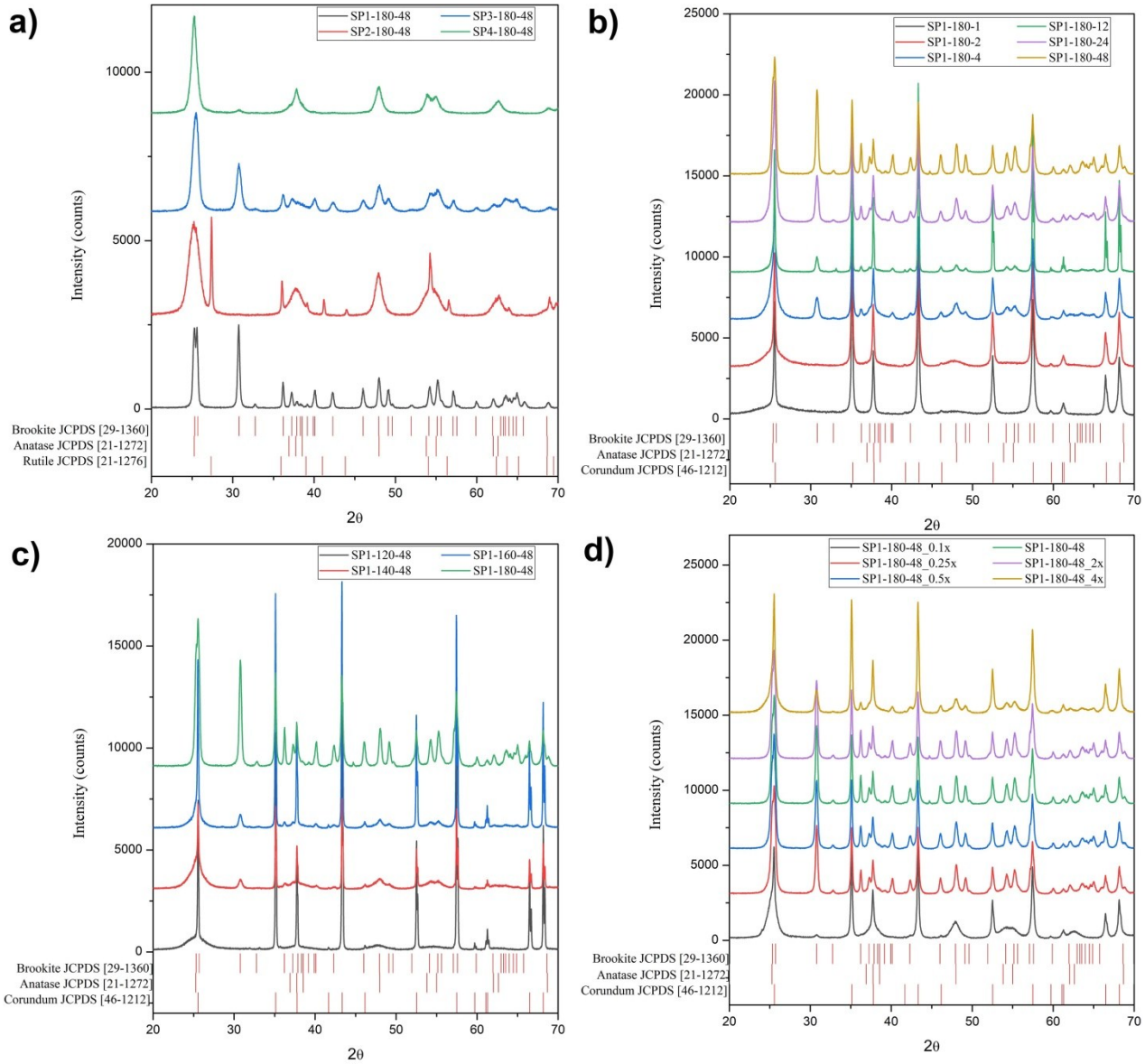


Fig. S2. XRD patterns of the samples prepared from different reaction mixtures (a); samples prepared by varying hydrothermal treatment duration (b); samples prepared by varying hydrothermal treatment temperature (c) and samples prepared by varying concentration (d).

The data in Table S1 correspond to Fig.s 1, 5, 7 and 8.

Table S1. Crystallite sizes and phase composition of the samples prepared by varying reaction mixture composition, duration of the synthesis, temperature and the concentration of titanium lactate precursor.

	Sample	Phase content, %				Particle size, nm		
		X-ray amorphous	anatase	brookite	rutile	anatase	brookite [a]	rutile
Precursor	SP1-180-48	11	0	89	0	-	72×34	-
	SP2-180-48	9	75	0	16	8	-	141
	SP3-180-48	11	5	84	0	33	60×18	-
	SP4-180-48	10	74	16	0	17	25×25	-
Time	SP1-180-1	100	0	0	0	-	-	-
	SP1-180-2	78	22	0	0	4	-	-
	SP1-180-4	42	15	43	0	4	24×11	-
	SP1-180-12	32	17	51	0	7	43×23	-
	SP1-180-24	27	5	69	0	9	58×32	-
Temp.	SP1-120-48	74	26	0	0	4	-	-
	SP1-140-48	31	31	38	0	7	26×17	-
	SP1-160-48	26	26	48	0	9	40×21	-
Concentration	SP1-180-48_0.1x	9	13	78	0	8	32×16	-
	SP1-180-48_0.25x	10	9	80	0	19	66×26	-
	SP1-180-48_0.5x	10	0	90	0	-	67×30	-
	SP1-180-48_2x	11	0	89	0	-	99×36	-
	SP1-180-48_4x	12	23	65	0	7	45×23	-

[a] – the crystallite size of brookite along and perpendicular to [001] directions.

2. Additional TEM images.

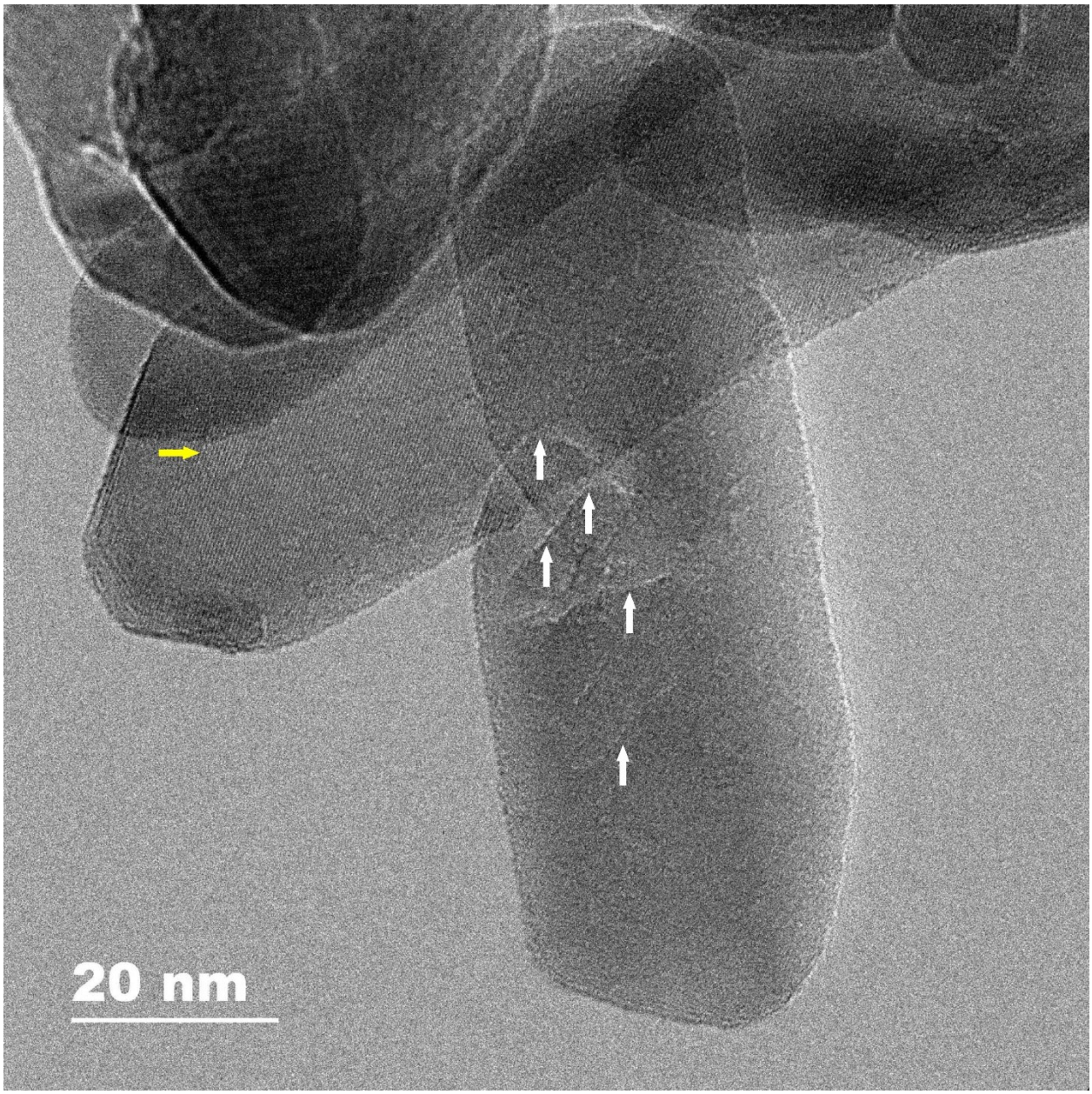


Fig. S3. TEM image of SP1-180-48 sample which was prepared by hydrothermal treatment of titanium lactate complex at 180 °C and pH 11 for 48 hours. The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

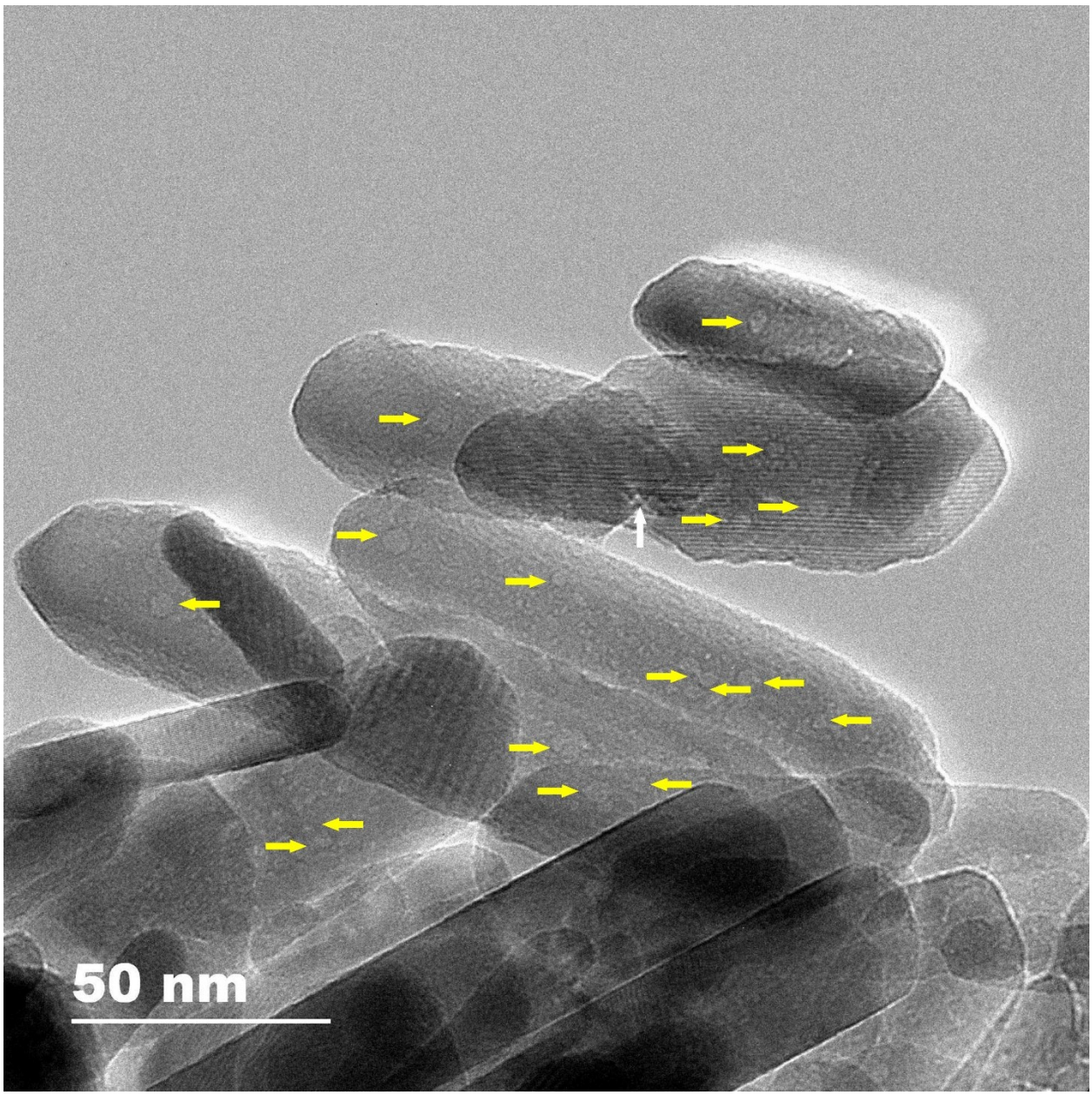


Fig. S4. TEM image of SP1-180-48 sample which was prepared by hydrothermal treatment of titanium lactate complex at 180 °C and pH 11 for 48 hours. The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

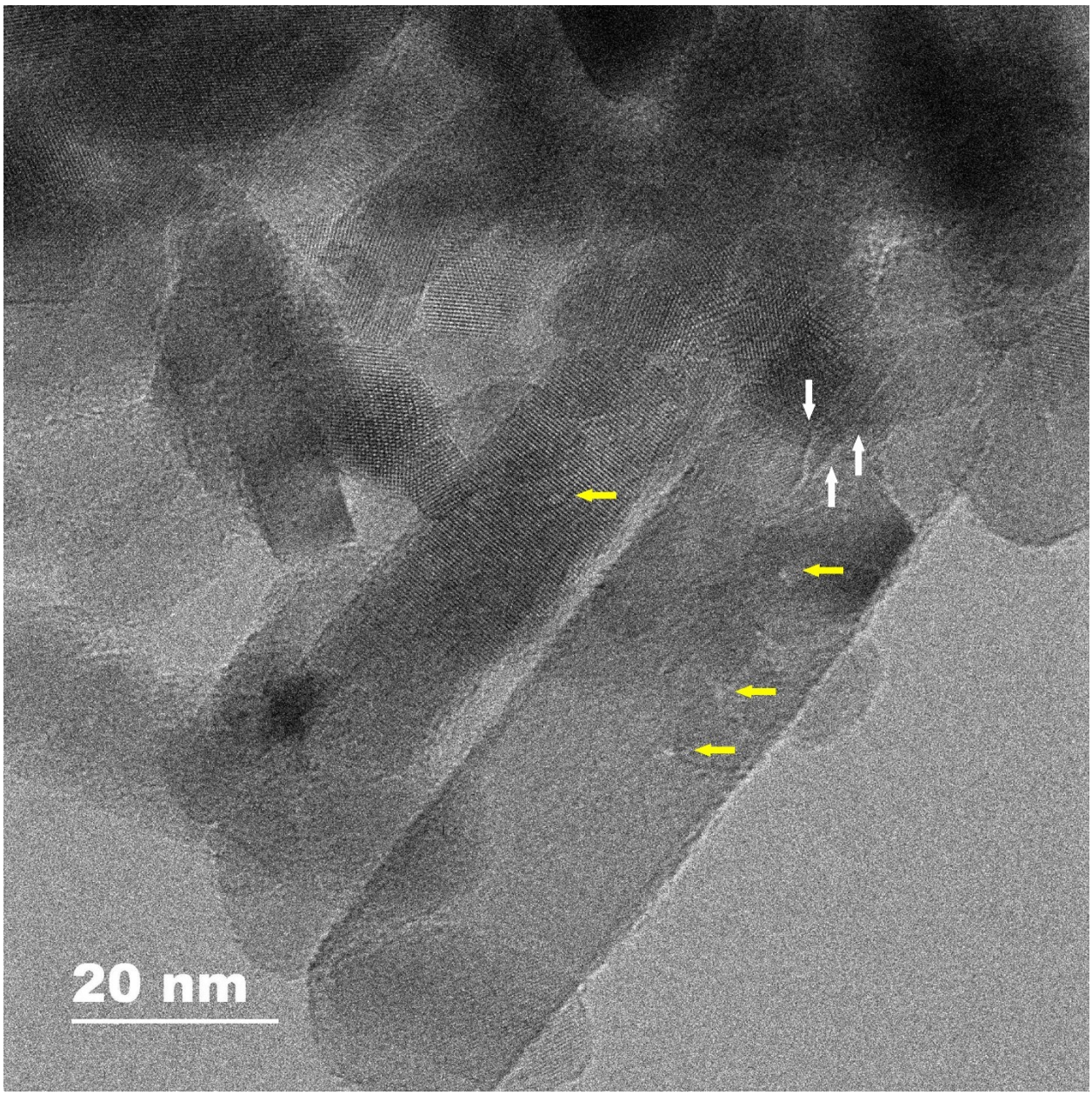


Fig. S5. TEM image of SP3-180-48 sample which was prepared by hydrothermal treatment of hydrated titanium oxide in the presence of lactate ions at 180 °C and pH 11 for 48 hours. The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

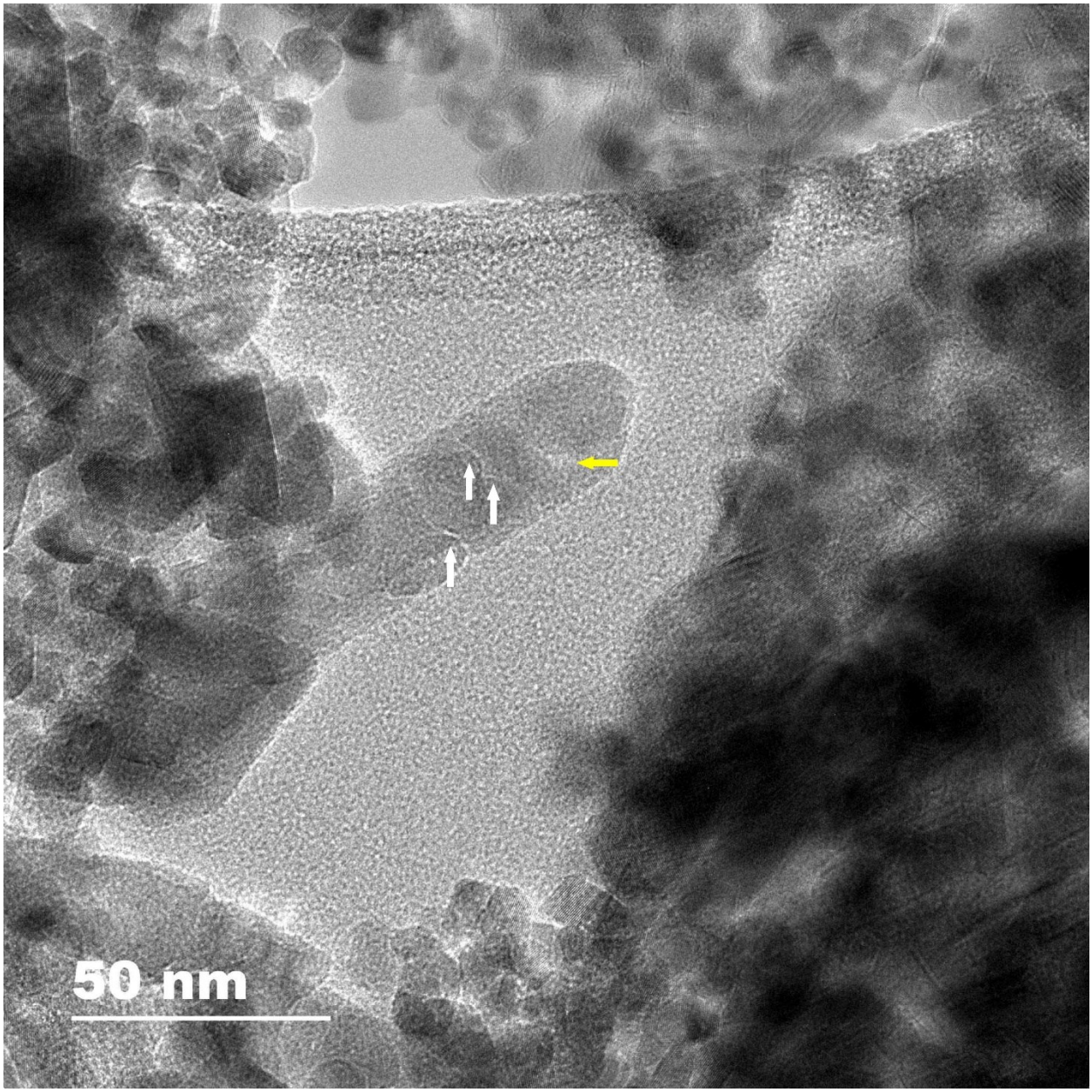


Fig. S6. TEM image of SP3-180-48 sample which was prepared by hydrothermal treatment of hydrated titanium oxide without lactate ions at 180 °C and pH 11 for 48 hours. The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

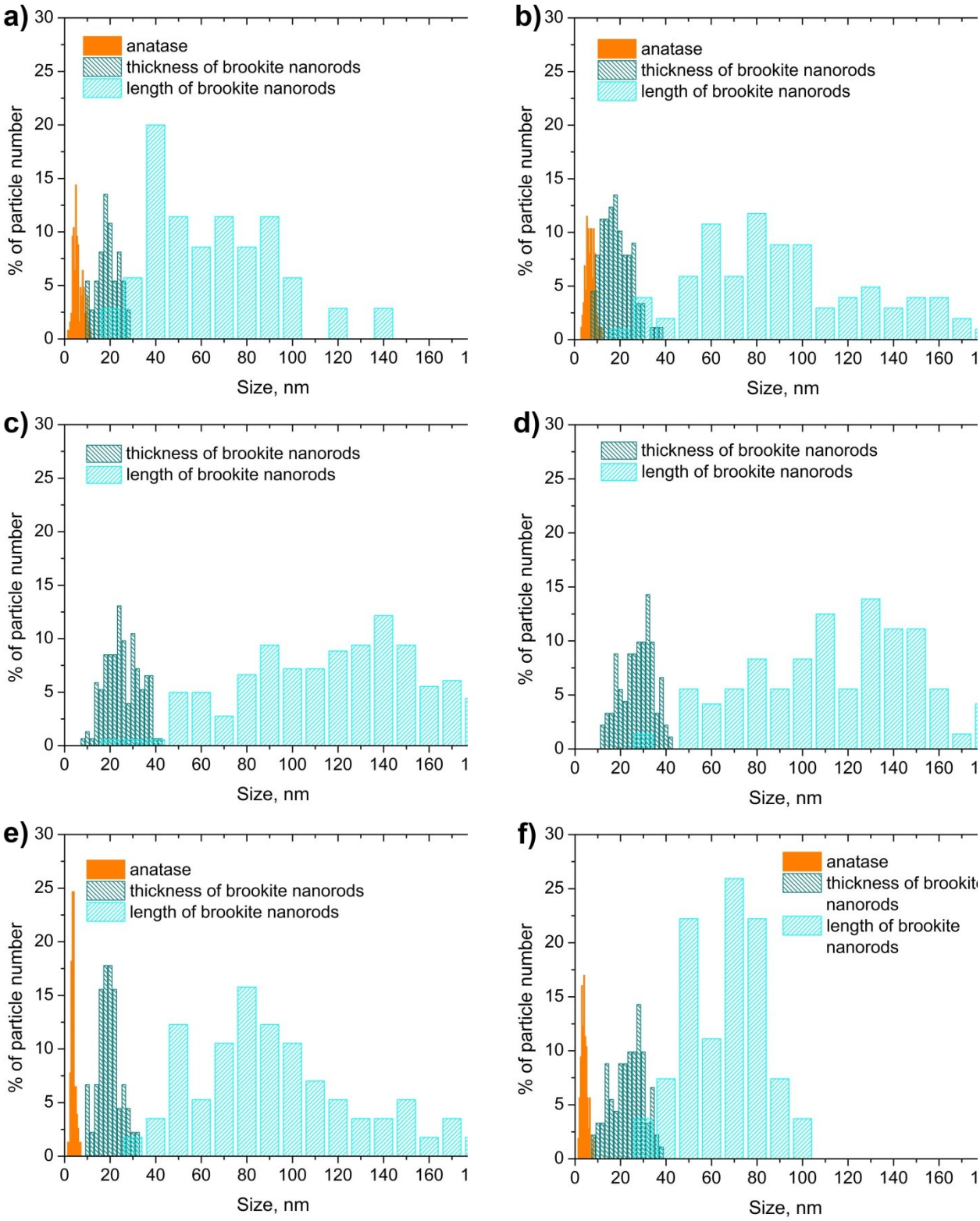
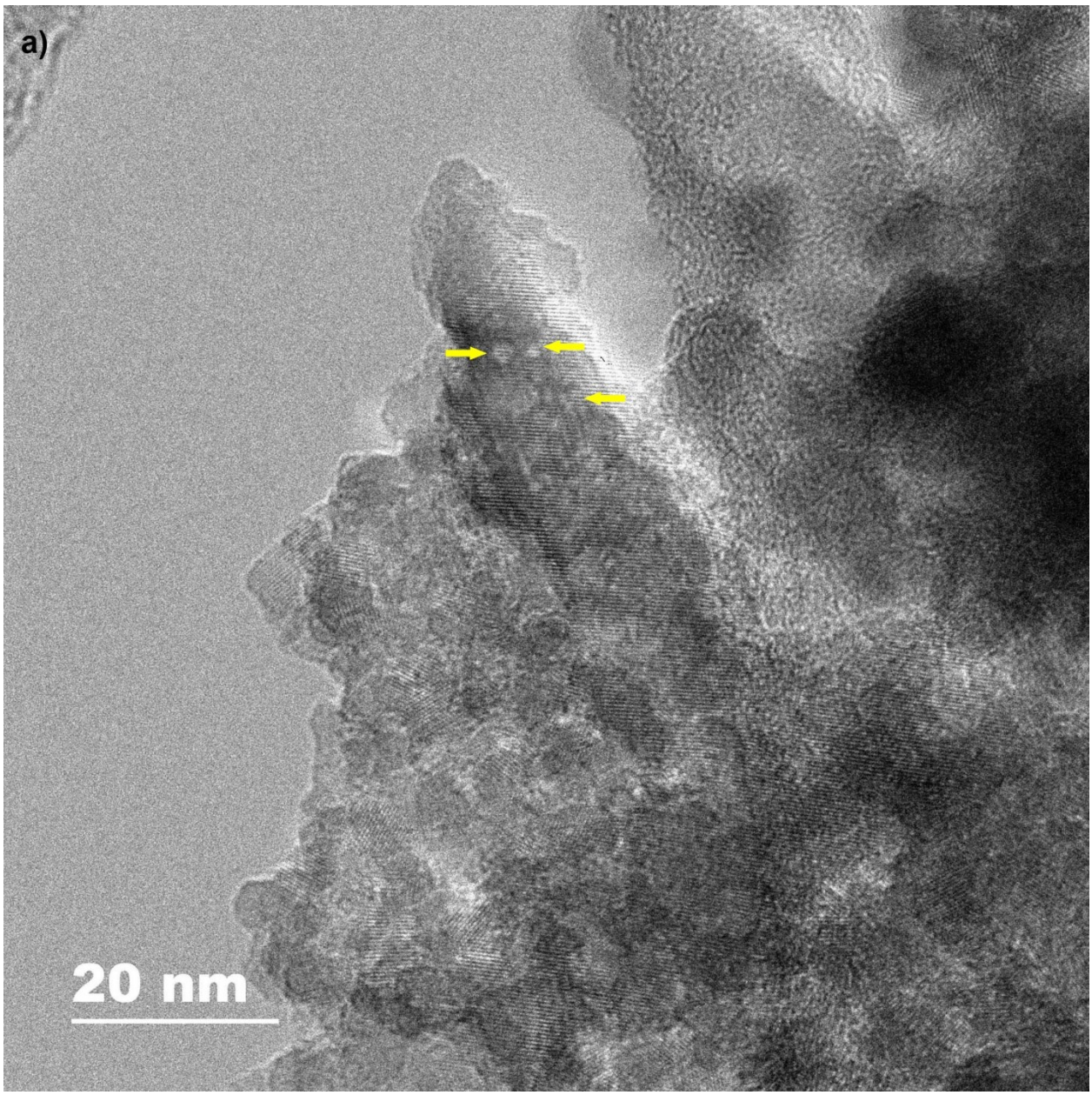
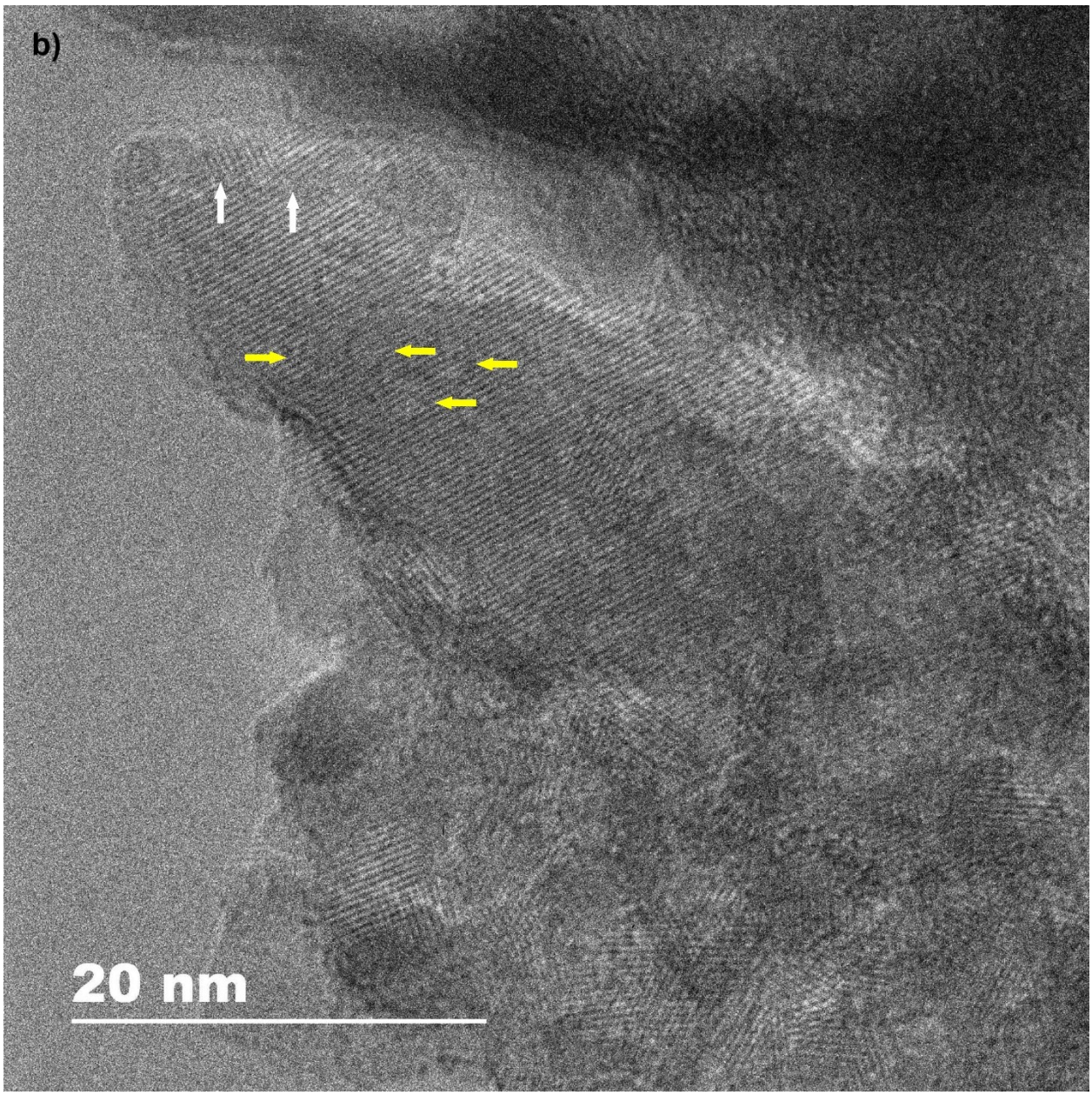


Fig. S7. Particle size distributions of anatase nanoparticles and brookite nanorods (thickness and length) for the samples consisting of pure brookite phase or a mixture of anatase and brookite: SP1-180-48_0.1x (a), SP1-180-48_0.25x (b), SP1-180-48_0.5x (c), SP1-180-48 (d), SP1-180-48_4x (e), SP1-180-4 (f).


a)
20 nm


b)
20 nm

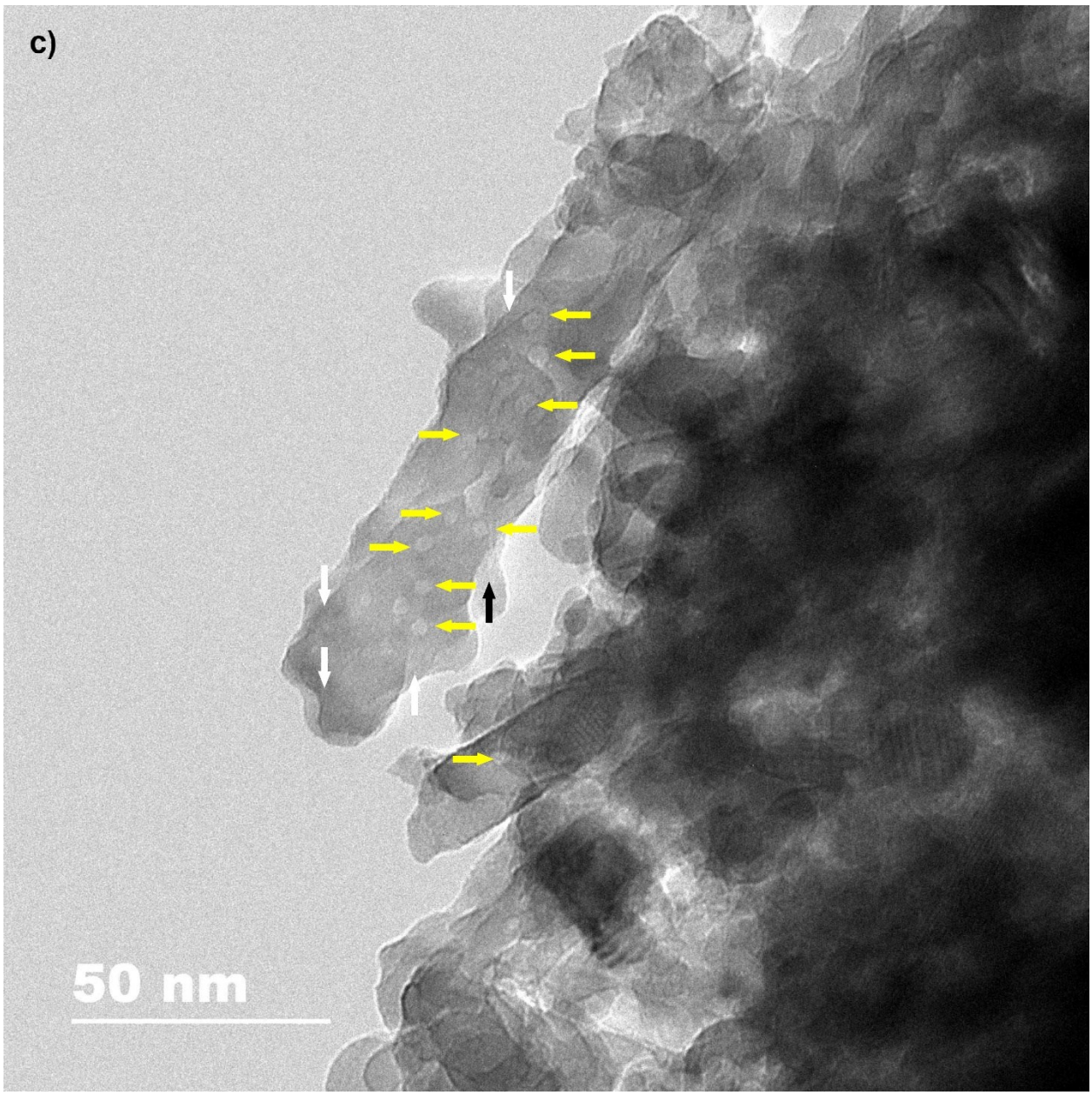


Fig. S8. SP1-180-4 sample which was prepared by hydrothermal treatment of titanium lactate complex at 180 °C and pH 11 for 4 hours. Initial stages of brookite particle formation. The particles of brookite at this stage already had a crystalline structure (a, b), while being imperfect, with poorly faceted shape with pores (c). The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

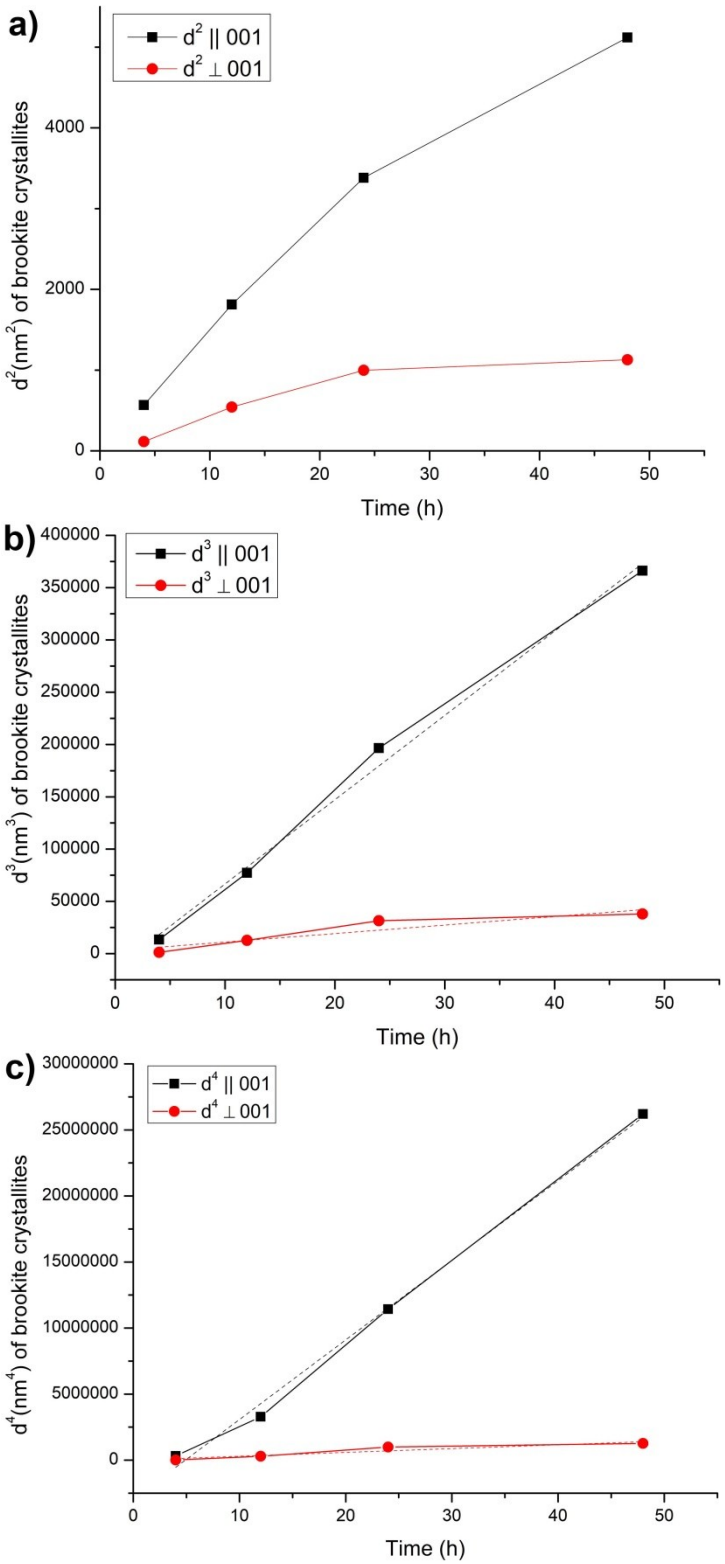


Fig. S9. Time dependencies of brookite crystallite sizes d^n. The series of samples SP1-180-*t* was prepared by hydrothermal treatment of titanium lactate complex at 180 °C and pH 11 with different durations of treatment. The dependencies are not linear for n=2 (both directions) (a), 3 (b) and 4 (perpendicular to 001) (c).

References

1. A. Le Bail, H. Duroy, J.L. Fourquet. *Mat. Res. Bull.*, 1988, **23**, 447–452.

2. V. Petricek, M. Dusek, L. Palatinus. Z. Kristellogr., 2014, **229**, 345-352.

3. V.A. Lebedev, D.A. Kozlov, I.V. Kolesnik, A.S. Poluboyarinov, W. Grünert, A.V. Garshev. *Applied Catalysis B: Environmental* 2016, **195,** 39–47.