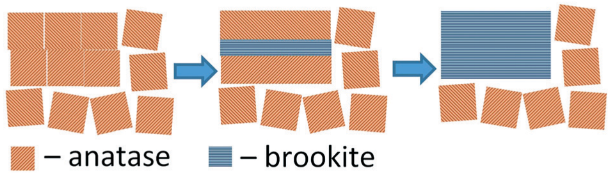
CrystEngComm c9ce00682f

We have presented the graphical abstract image and text for your article below. This briefly summarises your work, and will be presented with your article online.



Non-classical growth of brookite nanorods

Irina V. Kolesnik, Daniil A. Kozlov,
Anton S. Poluboyarinov, Alexey V. Garshev
and Vladimir K. Ivanov*

Under hydrothermal conditions, the formation of the brookite phase occurs due to the oriented attachment of anatase particles with subsequent recrystallization.

Please check this proof carefully. Our staff will not read it in detail after you have returned it.

Please send your corrections either as a copy of the proof PDF with electronic notes attached or as a list of corrections. **Do not edit the text within the PDF or send a revised manuscript** as we will not be able to apply your corrections. Corrections at this stage should be minor and not involve extensive changes.

Proof corrections must be returned as a single set of corrections, approved by all co-authors. No further corrections can be made after you have submitted your proof corrections as we will publish your article online as soon as possible after they are received.

Please ensure that:

- The spelling and format of all author names and affiliations are checked carefully. You can check how we have identified the authors' first and last names in the researcher information table on the next page. **Names will be indexed and cited as shown on the proof, so these must be correct.**
- Any funding bodies have been acknowledged appropriately and included both in the paper and in the funder information table on the next page.
- All of the editor's queries are answered.
- Any necessary attachments, such as updated images or ESI files, are provided.

Translation errors can occur during conversion to typesetting systems so you need to read the whole proof. In particular please check tables, equations, numerical data, figures and graphics, and references carefully.

Please return your **final** corrections, where possible within **48 hours** of receipt following the instructions in the proof notification email. If you require more time, please notify us by email to crystengcomm@rsc.org.

Funding information

Providing accurate funding information will enable us to help you comply with your funders' reporting mandates. Clear acknowledgement of funder support is an important consideration in funding evaluation and can increase your chances of securing funding in the future.

We work closely with Crossref to make your research discoverable through the Funding Data search tool (http://search.crossref.org/funding). Funding Data provides a reliable way to track the impact of the work that funders support. Accurate funder information will also help us (i) identify articles that are mandated to be deposited in **PubMed Central (PMC)** and deposit these on your behalf, and (ii) identify articles funded as part of the **CHORUS** initiative and display the Accepted Manuscript on our web site after an embargo period of 12 months.

Further information can be found on our webpage (http://rsc.li/funding-info).

What we do with funding information

We have combined the information you gave us on submission with the information in your acknowledgements. This will help ensure the funding information is as complete as possible and matches funders listed in the Crossref Funder Registry.

If a funding organisation you included in your acknowledgements or on submission of your article is not currently listed in the registry it will not appear in the table on this page. We can only deposit data if funders are already listed in the Crossref Funder Registry, but we will pass all funding information on to Crossref so that additional funders can be included in future.

Please check your funding information

The table below contains the information we will share with Crossref so that your article can be found *via* the Funding Data search tool. **Please check that the funder names and grant numbers in the table are correct and indicate if any changes are necessary to the Acknowledgements text.**

Funder name	Funder's main country of origin	Funder ID (for RSC use only)	Award/grant number
Russian Science Foundation	Russia	501100006769	17-73-10493

Researcher information

Please check that the researcher information in the table below is correct, including the spelling and formatting of all author names, and that the authors' first, middle and last names have been correctly identified. **Names will be indexed and cited as shown on the proof, so these must be correct.**

If any authors have ORCID or ResearcherID details that are not listed below, please provide these with your proof corrections. Please ensure that the ORCID and ResearcherID details listed below have been assigned to the correct author. Authors should have their own unique ORCID iD and should not use another researcher's, as errors will delay publication.

Please also update your account on our online manuscript submission system to add your ORCID details, which will then be automatically included in all future submissions. See here for step-by-step instructions and more information on author identifiers.

First (given) and middle name(s)	Last (family) name(s)	ResearcherID	ORCID
Irina V.	Kolesnik	N-6362-2016	0000-0002-1411-6691
Daniil A.	Kozlov		0000-0003-0620-8016
Anton S.	Poluboyarinov		
Alexey V.	Garshev		
Vladimir K.	Ivanov	H-4407-2011	0000-0003-2343-2140

Queries for the attention of the authors

Journal: **CrystEngComm**

Paper: **c9ce00682f**

Title: **Non-classical growth of brookite nanorods**

For your information: You can cite this article before you receive notification of the page numbers by using the following format: (authors), CrystEngComm, (year), DOI: 10.1039/c9ce00682f.

Editor's queries are marked on your proof like this Q1, Q2, etc. and for your convenience line numbers are indicated like this 5, 10, 15, ...

Please ensure that all queries are answered when returning your proof corrections so that publication of your article is not delayed.

Query Reference	Query	Remarks
Q1	Please confirm that the spelling and format of all author names is correct. Names will be indexed and cited as shown on the proof, so these must be correct. No late corrections can be made.	
Q2	"Naicker" is not cited as an author of ref. 5. Please indicate any changes that are required here.	
Q3	"Kaplan" is not cited as an author of ref. 2. Please indicate any changes that are required here.	
Q4	"Kandiel" is not cited as an author of ref. 11. Please indicate any changes that are required here.	
Q5	The caption to Fig. 1 has been altered for clarity, please check that the meaning is correct.	
Q6	The sentence beginning "The size range..." has been altered for clarity, please check that the meaning is correct.	
Q7	The sentence beginning "The suggested mechanism..." has been altered for clarity, please check that the meaning is correct.	
Q8	The sentence beginning "The facilities in..." has been altered for clarity, please check that the meaning is correct.	
Q9	Ref. 17: Please provide the initial(s) for the 3rd author.	

CrystEngComm

ROYAL SOCIETY OF CHEMISTRY

PAPER

Non-classical growth of brookite nanorods†

Q1 Cite this: DOI: 10.1039/c9ce00682f

Irina V. Kolesnik,[ab] Daniil A. Kozlov,[ab] Anton S. Poluboyarinov,[a] Alexey V. Garshev[ac] and Vladimir K. Ivanov*[ab]

Received 4th May 2019,
Accepted 18th August 2019

DOI: 10.1039/c9ce00682f

rsc.li/crystengcomm

To understand the growth processes of the brookite phase under hydrothermal conditions, several series of the samples were prepared, with varying temperatures, durations of the synthesis, precursor types and concentrations. A titanium lactate complex and amorphous hydrated titania were used as precursors. The samples were thoroughly characterized by XRD: integral intensities of the fitted peaks were used for the determination of the degree of crystallinity, phase composition and anisotropy of the particles. A series for which the duration of the synthesis was varied has shown that, at the initial stage, only amorphous and anatase phases were formed from the titanium lactate complex, while the brookite phase appeared after 4 hours of synthesis and its content grew with increasing synthesis time, at the expense of the anatase and amorphous phases. In all the cases when synthetic conditions allowed for brookite formation, the size of anatase crystallites was smaller than 19 nm, and the size of brookite particles was larger than 11 nm. A detailed HRTEM study of brookite particles has shown that they have pores and are built from several blocks. These results indicate that, under hydrothermal conditions, the formation of the brookite phase occurs due to a non-classical oriented attachment growth mechanism.

Introduction

Brookite remains one of the least studied crystalline modifications of titanium dioxide.[1,2] The lack of information on the properties of brookite is presumably caused by the absence of robust synthetic strategies for obtaining phase pure brookite. There are still only a few papers suggesting reproducible methods for preparing brookite not contaminated with other TiO_2 polymorphs.[1–4]

The synthesis of pure brookite without the admixture of anatase or rutile is complicated by thermodynamic properties of these phases. The only thermodynamically stable TiO_2 phase is rutile, while anatase and brookite may only be stabilized in the nanocrystalline state by an excess surface energy.[5,7–9] Thus, the phase composition of TiO_2 is strongly determined by nanoparticles' size, habits and surface adsorbates. According to existing reports, anatase is more stable than rutile when the particle size is less than 14 nm.[5] These data explain why anatase is typically a predominant product after synthesis under mild conditions. The simulations which were performed by Naicker *et al.* showed that, for smaller particles (2–6 nm), the surface energies of anatase and brookite are very similar.[5] Zhang *et al.* estimated the particle size range required for thermodynamic stability of brookite to be 11–35 nm,[9] while anatase is stable when the particles are smaller than 11 nm. In fact, anatase may transform into rutile without the formation of brookite.[5,6] It is also worth mentioning that the formation of nanoparticles, in many cases, occurs in a non-equilibrium regime, and kinetic factors may also affect the TiO_2 polymorph formation.

Most of the approaches to the synthesis of brookite comprise hydrothermal treatment of titanium compounds, namely hydrated titanium oxide[2] or Ti(IV) complexes containing peroxo- and carboxylate-ions as ligands.[10–17] The most attractive features of titanium complexes with alpha-hydroxy acids are high solubility and stability at room temperature in aqueous solutions.[10] These features allow for strictly controlled hydrolysis in a wide temperature and pH range, and for the preparation of various modifications of TiO_2 (anatase, brookite, rutile and their mixtures).

The formation of the specific crystalline modification of titania is supposed to be driven by topochemical reactions, and thus would depend on the molecular structure of oligomers which are formed at the initial stage of precursor hydrolysis.[16] However, this hypothesis seems to be inconsistent with a well-known thermodynamic model of phase stability of TiO_2 polymorphs which has been mentioned above.[8,9] Analyzing the growth of brookite from this point of view, it is not clear how brookite seeds can be formed from hydrolyzed carboxylate complexes. Since brookite is stable in the size range 11–35 nm, very small brookite particles are less stable than

---

[a] Lomonosov Moscow State University, Leninskie Gory, 1, Moscow, 119991, Russia
[b] Kurnakov Institute of General and Inorganic Chemistry of RAS, Leninskii Ave. 31, Moscow, 119991, Russia. E-mail: van@igic.ras.ru
[c] Baikov Institute of Metallurgy and Material Science RAS, Leninskii Ave, 49, Moscow, 119334, Russia

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ce00682f

anatase.[8] In view of this evident difference, it is important to obtain a deeper insight into the mechanism of brookite formation.

In this paper, brookite formation under hydrothermal conditions was studied in detail. Analysis of the dependence of the phase composition of TiO_2 on the composition and concentration of precursors, pH, temperature and duration of treatment allowed us to deduce the most probable formation mechanism of this unusual TiO_2 polymorph.

Experimental

Synthesis

A titanium lactate complex and hydrated titanium oxide $TiO_2 \cdot xH_2O$ were used as the precursors for TiO_2 hydrothermal synthesis. The titanium lactate complex was prepared as follows: 17 ml of titanium butoxide (Sigma Aldrich, 97%) was added to a mixture of 16 ml of deionized water and 14 ml of lactic acid (Sigma Aldrich, 85%) and carefully heated until a clear solution was formed. Butanol was then removed by evaporation.

In the synthesis which resulted in a pure brookite phase, 4.86 g of urea (Sigma Aldrich, 95.5%) and 10 ml of the solution of the titanium lactate complex were dissolved in deionized water to form 24 ml of clear solution. The final concentration of Ti in this solution was 0.0021 M. It was transferred into a Teflon-lined, stainless steel autoclave (total volume 60 ml) and hydrothermally treated at 180 °C for 48 hours. A white precipitate was collected by centrifugation, washed four times with water and once by ethanol, and dried in air at room temperature overnight. The sample is hereafter referred to as **SP1-180-48**.

To study the influence of the synthesis parameters, the temperature and the duration of the hydrothermal treatment, and concentrations of the precursors, were varied. The corresponding titania samples are hereafter denoted as **SP1-*T*-*t***, where ***T*** is the temperature in °C and ***t*** is the treatment duration in hours. The samples with different concentrations of the precursor are denoted as **SP1-180-48-*nx***, where ***n*** is a factor of the concentration change. In this way, the samples with Ti concentrations of 0.0002 M, 0.0005 M, 0.0011 M, 0.0042 M and 0.0084 M were prepared.

To study the role of each precursor, one more series of the samples was prepared. For sample SP2-180-48, only the titanium lactate complex was subjected to hydrothermal treatment. To prepare SP3-180-48 and SP4-180-48 samples, amorphous hydrated titania was used as a precursor instead of the titanium lactate complex. 1.7 ml of titanium butoxide was hydrolyzed with 30 ml of water for 3 hours, and then the formed white precipitate was centrifuged. This led to the formation of amorphous hydrated titania, which showed no reflections on an XRD pattern. In the case of the SP4-180-48 sample, the precipitate was carefully redispersed in 24 ml of 6 M urea solution. To prepare the SP4-180-48 sample, the precipitate was carefully redispersed in 24 ml of the solution which contained 6 M urea and 0.0667 M lactic acid. Hydrothermal treatment of amorphous titania samples was performed at 180 °C for 48 hours. Upon completion of the synthesis, the pH was measured using an Ecotest-120 pH meter. Dried precipitates were weighed and analyzed by thermogravimetry to determine the TiO_2 yield. The yield and pH of the mother liquors are presented in Table 1.

Characterization

Thermal analysis was performed using a STA 409 PC Luxx (Netzsch) analyzer. The measurements were performed using Al_2O_3 crucibles under an air flow of 30 ml min^{-1} and with a heating rate of 10 °C min^{-1} up to 800 °C. The weight loss in all cases ended at 700 °C. Thermal analysis data were further used to calculate the yield of TiO_2.

Raman spectra were acquired using an inVia Raman spectrometer (Renishaw) coupled to a Leica DMLM optical microscope with a 100× objective. Measurements were performed at room temperature in the Raman shift frequency range of 100–1460 cm^{-1} using a 50 mW 514 nm argon laser. The Raman spectrometer was calibrated against the F_{1g} line of Si at 520.2 cm^{-1} as a reference. The bands of TiO_2 were assigned according to the literature.[14,18,19]

The microstructure of the samples was characterized using transmission electron microscopy (TEM, Zeiss Libra 200 MC). Selected area electron diffraction (SAED) was performed using the 5 μm selective aperture. X-ray diffraction (XRD) patterns were collected using a Rigaku D/MAX 2500 diffractometer ($\theta/2\theta$ Bragg–Brentano reflection geometry) with a scintillation counter. All the measurements were performed with CuK_α radiation generated on a rotating Cu anode (45 kV, 250 mA). XRD patterns were obtained in the 20–70° 2θ range with a 0.02° step at 4 s per step. XRD profiles were fitted using JANA2006 software.[20] Integral intensities of the fitted peaks were used to determine the degree of crystallinity. The determination of the phase composition was performed using the ICDD PDF-2 database. The Le Bail method of full profile analysis[21] was used for the determination of integral intensities. The full details of the XRD experiments are provided elsewhere[22] (see also the ESI,† Fig. S1 and S2).

Results and discussion

To find the key factors affecting the phase composition of titania, a series of experiments were performed in which reaction parameters were varied, including the comparison and the concentration of the precursors, and the temperature and pH of the medium. The composition and the pH of the solutions are presented in Table 1. After hydrothermal treatment, the pH was close to 11 in all the cases when urea was added into the medium. Here, urea served as the source of OH ions.[11] When urea was not added, the pH was 3.3.

The results of the quantitative phase analysis and crystallite size determination using XRD data are presented in Fig. 1 and Table S1.† In basic media, when urea was added to the reaction mixture, the pure brookite phase was formed

Table 1 The precursors, composition of reaction mixtures, pH of mother liquors after synthesis and reaction yields for SP1-180-48, SP2-180-48, SP3-180-48 and SP4-180-48 samples

Sample name	Precursor	Urea, 6M	Lactic acid	pH of the mother liquor after hydrothermal treatment	TiO_2 yield, %
SP1-180-48	Ti lactate complex	+	n/a	11	74
SP2-180-48	Ti lactate complex	—	n/a	3	39
SP3-180-48	$TiO_2{\cdot}xH_2O$	+	+	11	79
SP4-180-48	$TiO_2{\cdot}xH_2O$	+	—	11	68

(SP1-180-48, SP3-180-48, and SP4-180-48 samples). When the synthesis was performed in the acidic medium, a mixture of anatase and rutile was formed. Thus, the basic conditions were quite important for the formation of the brookite phase. This conclusion is in good agreement with previous reports.[2,8,12] For instance, formation of brookite in a basic medium in the absence of α-hydroxy acids was also observed by Kaplan *et al.*, who obtained pure brookite under hydrothermal conditions at 200 °C.[2] Kandiel *et al.* showed that the pure brookite phase is formed from the lactate complex when the concentration of urea is 6M and more, whereas lower concentrations of urea promote the formation of a mixture of anatase and brookite.[11] Obviously, a high concentration of urea provides high enough pH for the formation of the brookite phase. Similarly, brookite can be obtained from the Ti(IV) glycolate complex at pH 10 and 200 °C.[16]

It is worth mentioning that the brookite phase also forms when the sol of hydrated titanium oxide is used as a precursor. The starting sol consists of X-ray amorphous particles, and the maxima in the corresponding Raman spectrum are very broad and do not match the maxima of brookite, anatase or rutile, but are placed between the positions of the peaks of these phases (Fig. 2). Supposedly, this X-ray amorphous phase is also built from TiO_6 octahedra, which are characteristic for TiO_2 crystalline phases, while these octahedra are randomly connected to one another.

Upon hydrothermal treatment of the hydrated titanium oxide sol at 180 °C for 48 hours, in the presence of 6 M urea at pH 10, the amorphous phase crystallizes, giving a mixture of anatase (74%) and brookite (16%). Thus, the formation of brookite is possible even in the absence of lactate ions. Moreover, small amounts of brookite can also form after the hydrolysis of titanium alkoxide, with subsequent annealing in air and treatment with hydrazine.[23] When lactate ions are introduced to the solution, the fraction of brookite rises to 84%. The reaction yields in these two cases are 68% and 79%, respectively. Thus, one can propose that lactate ions promote the formation of the brookite phase in an alkaline medium due to recrystallization of anatase and amorphous phases, while the presence of the titanium lactate complex as a precursor at the initial stage is not so important for brookite phase formation.

This supposition does not corroborate the mechanisms of brookite formation which have been proposed previously.[12,16] These mechanisms suggest that the seeds of certain TiO_2 phases are formed *via* hydrolysis of certain titanium carboxylate complexes. The primary crystals of TiO_2 polymorphs are supposed to have an atomic structure resembling the structure of the precursors and/or oligomers formed at primary hydrolysis stages. These seeds could act as a substrate for the further growth of the particles of a certain TiO_2 phase. However, in our experiments, the formation of the brookite phase occurred even from the precursor, which had an anatase-like

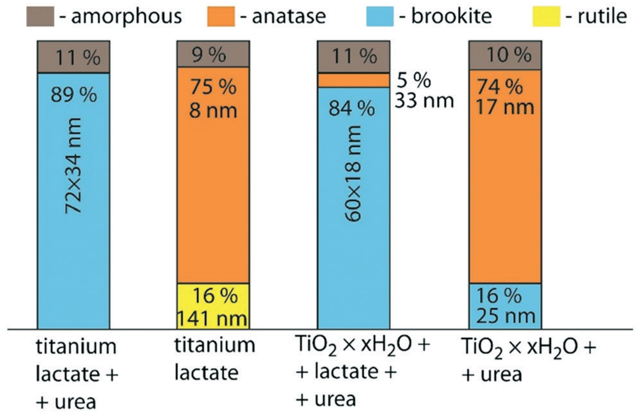


Fig. 1 Phase composition and crystallite sizes of the samples prepared from different reaction mixtures. Reaction mixture composition, time of the synthesis – 48 hours, temperature – 180 °C, Ti concentration – 0.0021 M.

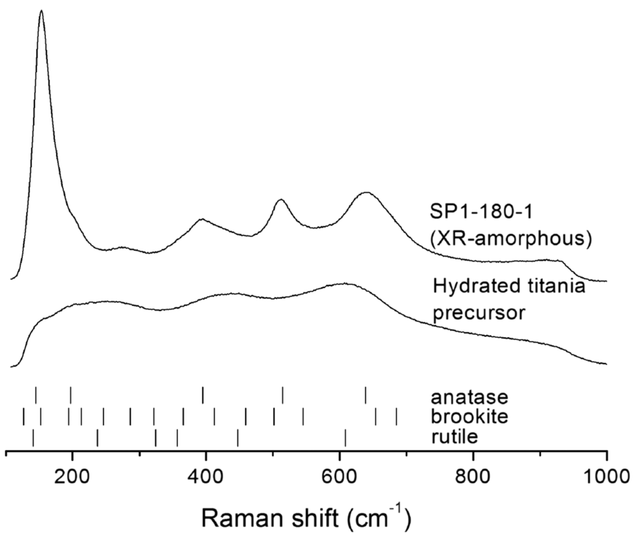


Fig. 2 Raman spectra of X-ray amorphous titanium oxide samples. Hydrated titanium oxide was obtained by hydrolysis of $Ti(O^nBu)_4$ in aqueous media; the SP1-180-1 sample was obtained by hydrolysis of the titanium lactate complex under hydrothermal conditions at pH 11.

structure. The crystallization of brookite from titanyl sulphate and titanium chloride in the presence of carboxylates has also been observed by many other researchers.[24–28]

The results of TEM analysis suggest a possible route for the formation of brookite from anatase. Fig. 3a, S3 and S4† show that sample SP1-180-48 consists of rod-like particles with inclined edges. As this sample contains only the brookite phase, it is possible to conclude that the rod-like shape is typical for brookite formation under hydrothermal conditions in an alkaline medium in the presence of lactate ions.

Sample SP3-180-48, which was synthesized in an alkaline medium from the sol of hydrated TiO_2 in the presence of lactate ions, contained rod-like particles similar to those observed in the SP1-180-48 sample, but having a smaller size, which probably also corresponded to the brookite phase (Fig. 3b). For anatase particles, the crystallite size was 33 nm, and it is somewhat difficult to distinguish them from brookite particles. Thus, the SP4-180-48 sample consisted of two types of particles, and according to XRD it contained two crystalline TiO_2 phases (Fig. 3c). The larger particles probably corresponded to the brookite phase. These particles contain a large number of defects and pores, and are typically built from several blocks. This block structure can also be observed in some particles in the SP1-180-48 (Fig. S3 and S4†) and SP3-180-48 (Fig. S5 and S6†) samples. The presence of pores in some crystals provides additional evidence of their block structure.[29]

Another piece of evidence of the block structure of the brookite nanorods came from the particle size distribution in the TEM images. The particle size distributions are presented in Fig. S7.† For each sample, the particle sizes of 100 to 300 particles were measured. Brookite nanorods appeared to have very wide size distributions in the longitudinal dimension. The corresponding values were found to be several times larger than the sizes of crystallites calculated by the Scherrer equation from the XRD results (Table S1†).

The assumption concerning the block structure of brookite particles is also confirmed by the presence of streaks in diffraction patterns in both [004] and [0–21] directions. These streaks were supposed to be a feature of particles with a block structure.[29–31] Additionally, HRTEM images and diffraction patterns of the samples SP1-160-48 and SP1160-100 (Fig. 4) were analyzed and the direction of brookite particles' growth was identified. In Fig. 4a, a brookite particle is viewed along the [001] zone axis. In the corresponding diffraction pattern (Fig. 4b), the [001] zone with (210) and (200) basis vectors was identified. The vectors' lengths were in strong accordance with the brookite unit cell parameters a = 9.19 Å, b = 5.46 Å, and c = 5.14 Å. In the diffraction pattern (Fig. 4d) corresponding to the TEM image (Fig. 4c), the particle is viewed along the [120] direction, with (−210) and (001) basis vectors and the same unit cell parameters. Thus, the longitudinal direction of the brookite nanorod is [001], which coincides with the data reported by Kandiel *et al.*[12] According to Fig. 4a, the side planes of the brookite particles were {210}, corresponding to the minimum brookite surface energy.[25]

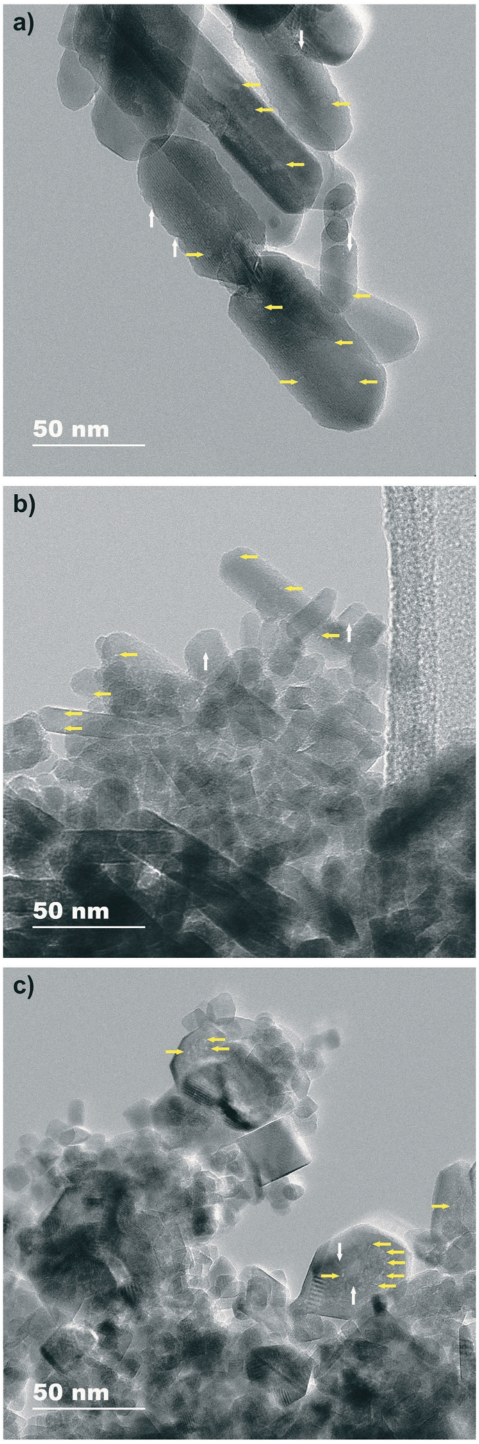


Fig. 3 TEM images of titania samples. (a) SP1-180-48 sample prepared by hydrothermal treatment of the titanium lactate complex at pH 11 consists of the brookite phase (rod-like particles with inclined edges). (b) SP3-180-48 sample prepared by hydrothermal treatment of hydrated titanium oxide in the presence of lactate ions at pH 11 consists of the brookite phase (rod-like particles with inclined edges) and 5% anatase phase. (c) SP4-180-48 sample prepared by hydrothermal treatment of hydrated titanium oxide without lactate at pH 11; consists of the brookite phase (particles with inclined edges) and anatase particles (smaller particles). All the syntheses were performed at 180 °C for 48 hours under basic conditions. The pores in brookite crystals are marked with yellow horizontal arrows, and the defects are marked with white vertical arrows.

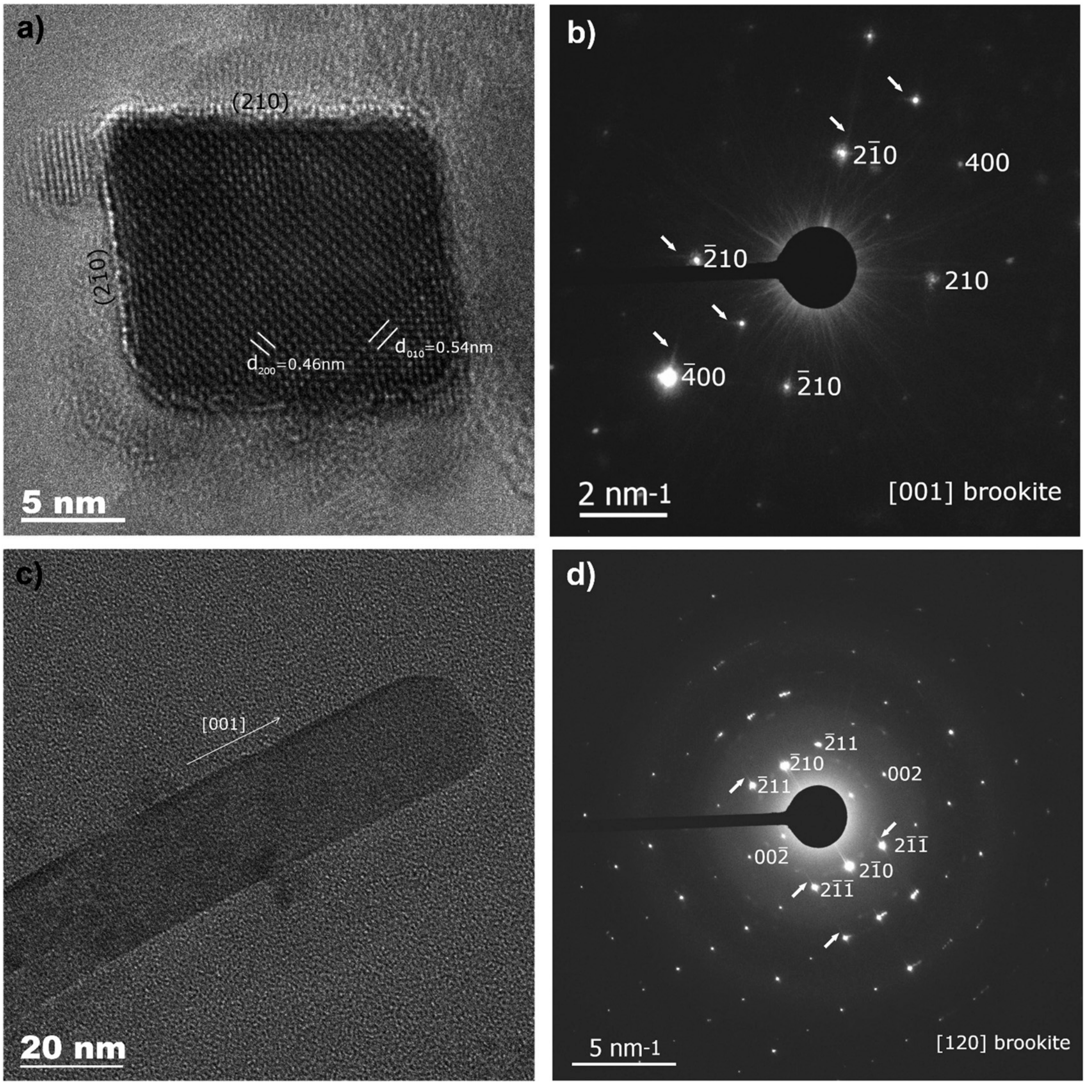


Fig. 4 TEM images of a single brookite particle (sample SP1-160-48). Bright field (a) and SAED patterns (b); TEM image of a single brookite particle (sample SP1-160-100). Bright field (c) and SAED patterns (d). Streaks in the diffraction patterns are marked with arrows.

Thus, based on the TEM images and electron diffraction data, one can propose that larger brookite particles are formed by merging small anatase particles. It is likely that, at the initial stage of synthesis, anatase particles orient themselves with respect to the neighbouring particles' orientation, and then fuse, and at the final stage the phase transition from anatase to brookite occurs. The predominant mechanism of brookite growth under these conditions is therefore the oriented attachment of anatase particles with the subsequent phase transition and possible Ostwald ripening of the particles. The presence of lactate ions and alkaline medium were found to be important for such a growth mechanism.

The formation of the brookite phase in twins of anatase crystals, as well as oriented attachment and phase transition from anatase to brookite, were studied by Penn and Banfield.[32] They have shown that the mutual attachment of anatase surfaces leads to twinning on {112} and intergrowth on (001) and {001} on the boundary of two anatase particles. The brookite phase may nucleate on this boundary, since anatase and brookite have similar fragments in their crystalline lattices, and the {112} anatase twin interface actually contains one unit cell of brookite. The activation barrier for anatase–brookite transformation is thus quite low, because the energy is only needed to move TiO_6 octahedra to neighbouring positions. Penn and Banfield also mentioned that the adsorption of ions on anatase seeds and lattice strain may influence phase transitions because of the change of surface energy. When the energies of anatase and brookite crystals are close to each other, the transition from anatase to brookite may be promoted by tiny changes in surface energy. Under our experimental conditions, the high pH and the presence of lactate ions adsorbed on the surface of anatase seeds are among the factors encouraging brookite formation.

It has been shown previously that the adsorption of carboxylic acids on the surface of anatase particles strongly influences particle–particle interaction. The presence of carboxylate ions in neutral media makes the suspensions of anatase much more stable.[33,34] Organic acids may also adsorb on the surface of anatase seeds,[35] so the fast aggregation is hindered, providing the possibility of oriented attachment of anatase particles, which further leads to the formation of the brookite phase at the boundary and further phase transition in anatase primary particles.

To understand in detail the growth and the structure of the seeds, a series of samples in the presence of 6 M urea at 180 °C, with different treatment durations, were studied. The phase composition and the crystallite sizes are provided in Fig. 5 and in Table S1.† At the initial stage, upon hydrothermal treatment for 1 hour (sample SP1-180-1), the formed precipitate was X-ray amorphous, being probably a hydrated titanium dioxide. According to the TEM data (Fig. 6a), the sample consisted of unfaceted particles of 4–5 nm size. The bands in the Raman spectrum of this sample are identical to those of anatase (Fig. 2). Thus, at the very beginning of the synthesis, hydrolysis of the titanium lactate complex led to the formation of X-ray amorphous hydrated TiO_2 with an anatase-like structure, whereas no peaks of the brookite phase can be observed. It is worth mentioning that the nanoparticles with the anatase structure were observed upon titanium lactate complex decomposition under very mild conditions.[36]

The next process taking place during hydrothermal synthesis was the crystallization of anatase. The SP1-180-2 sample which was hydrothermally treated for 2 hours already contained 22% anatase. Further hydrothermal treatment led to the formation of both anatase and brookite. Hydrothermal treatment for 4 hours produced large, rod-like particles, with small particles adhering to their surface (Fig. 6b and S8†). The smaller particles consisted of anatase and the bigger particles consisted of brookite. At this intermediate stage, brookite particles consisted of several blocks.

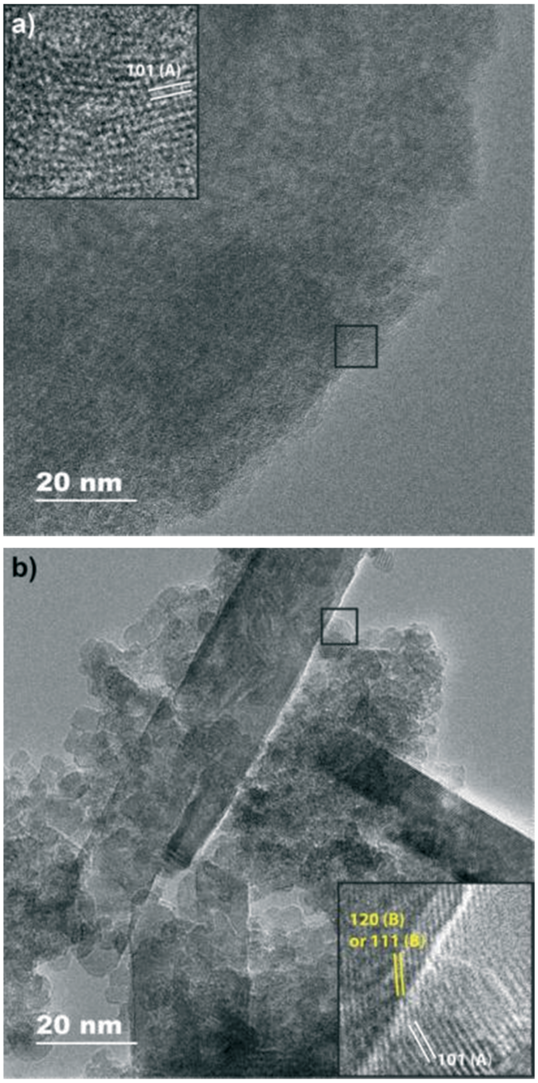


Fig. 6 TEM image of the SP1-180-1 sample prepared by hydrothermal treatment of the titanium lactate complex at 180 °C for 1 hour (a) and the SP1-180-4 sample prepared under the same conditions for 4 hours (b) at basic pH. "A" corresponds to the anatase phase and "B" corresponds to the brookite phase.

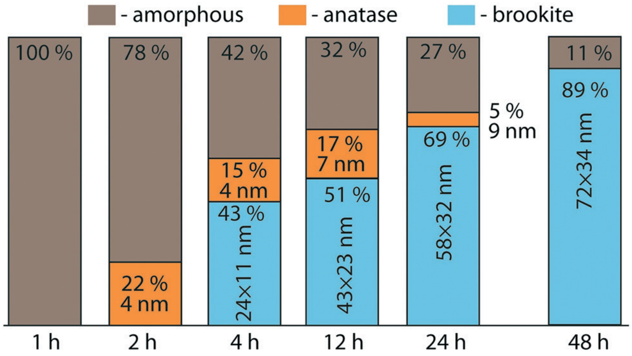


Fig. 5 Crystallite sizes and phase composition of the samples prepared by varying the hydrothermal treatment duration. Temperature was set at 180 °C, titanium lactate (C = 0.0021 M) was used as a precursor, pH 11.

Upon the increase in the duration of hydrothermal treatment, the content of anatase decreased, with a simultaneous increase in the content of brookite. The sample treated for 48 hours contained only the pure brookite phase. This series of experiments clearly demonstrates that, at the initial stage, the anatase phase is formed and then the formation of brookite takes place. Anatase particles act as building blocks for brookite, and after 48 hours they are totally converted into the brookite phase.

The formation of the primary anatase particles and their subsequent transformation to larger brookite particles agree well with thermodynamic considerations on the stability of TiO_2 phases. As has been shown previously,[9] the stability of TiO_2 polymorphs depends on the particle size, demonstrated as follows: anatase is stable when the particles are smaller than 11 nm, and brookite is stable when the particle size is between 11 and 35 nm. The results of our experiments agree well with this model. In all cases when synthetic conditions allow for partial or complete anatase-to-brookite transformation, the size of anatase crystallites did not exceed 19 nm, and in no cases was the size of brookite less than 11 nm. These data provide an additional argument for the oriented attachment growth mechanism of brookite.

Recently, Finnegan *et al.* studied the growth of anatase and anatase–brookite mixed samples, and found that the growth mechanism of the anatase phase depends strongly on the pH.[37] In acidic media, oriented attachment prevails, whereas under basic conditions Ostwald ripening takes place. In the intermediate region, both mechanisms co-exist. Finnegan *et al.* suggested an approach which makes it possible to distinguish between these two mechanisms. If the particles grow due to Ostwald ripening, the particle diameter should depend on the time as follows:

$$d^n = d_0^n + kt$$

where d_0 is the initial average diameter of the particle, k is a temperature-dependent constant and t is the time. The power coefficient n depends on the limitations on particles' growth: when n = 2, crystal growth is limited by the attachment of ions on the particle surface; when n = 3, the growth is controlled by the volume diffusion of ions; and when n = 4, the grain boundary diffusion controls the growth.[38,39] After linear fitting of the graphs d^n *vs.* t, we have found that, for the crystallite size in the direction perpendicular to [001], all the fits are not good, whereas in the [001] direction the linear fit is good enough (ESI,† Fig. S9†). These considerations support the oriented attachment mechanism of brookite growth, while Ostwald ripening cannot be completely excluded.

The solubility of titanium oxide under basic conditions is quite low (at 25 °C and pH 11, the solubility of titania is 1.1 × 10^{-9} mol L^{-1} (ref. 40)), but it can increase considerably at 180 °C, especially in the presence of bidentate lactate ions. Thus, anatase and amorphous TiO_2 may dissolve and then redeposit on the surface of the brookite phase which was already formed due to the oriented attachment of anatase particles and their recrystallization.

To find more arguments pro and contra the oriented attachment mechanism of brookite formation, the influence of temperature on the crystallite size and phase composition of TiO_2 samples has been studied. A series of samples were prepared by hydrothermal treatment at temperatures from 120 °C to 180 °C for 48 hours in the presence of 6 M urea.

The brookite content increases with an increase in temperature (Fig. 7, Table S1†). At higher temperatures, the colloidal system becomes less stable and the oriented attachment of the particles becomes more favourable. As a result, the content of brookite at higher temperatures increases. The increase of the brookite content with the increase in temperature agrees well with our hypothesis concerning the oriented attachment growth mechanism of brookite from small primary particles of anatase and X-ray amorphous TiO_2.

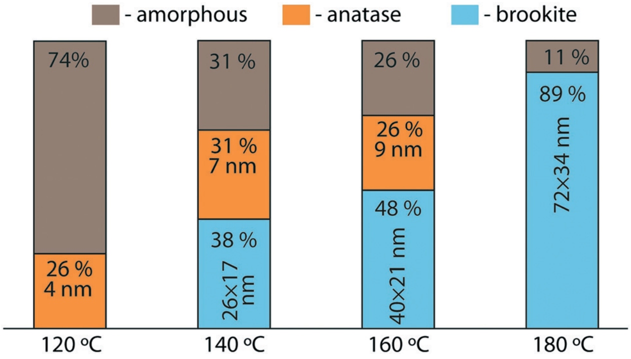


Fig. 7 Crystallite sizes and phase composition of the samples prepared by varying the hydrothermal treatment temperature. Time was set at 48 hours, titanium lactate (*C* = 0.0021 M) was used as a precursor, pH 11.

The brookite content was also found to depend on the titanium lactate precursor concentration. A series of TiO_2 samples were prepared using different concentrations of titanium. The duration, temperature and pH of the synthesis were chosen to promote the brookite formation (48 hours, 180 °C, pH 11).

The phase composition of the thus obtained samples is presented in Fig. 8 and Table S1.† At low concentrations of the lactate precursor, both anatase and brookite were present in the samples. In the optimal concentration range (0.0011–0.0042 M), the only TiO_2 phase formed was brookite. A further increase in the concentration of the titanium lactate precursor again led to the formation of a mixture of anatase and brookite. The observed changes in the phase composition of the samples depending on the precursor concentration are also in line with the oriented attachment model. At the first stage of hydrolysis (during the first hour), the titanium lactate complex hydrolyses and semi-amorphous TiO_2 particles with an anatase-like structure are formed. When low concentrations of the precursor are used, the attachment of TiO_2 anatase particles is hindered due to the low probability of particle collision. Next, in the intermediate concentration range, the concentration of TiO_2 anatase nanoparticles is high enough to cause a high probability of particle collision and attachment. Finally, synthesis from a concentrated titanium lactate solution results in the formation of a viscous gel-like

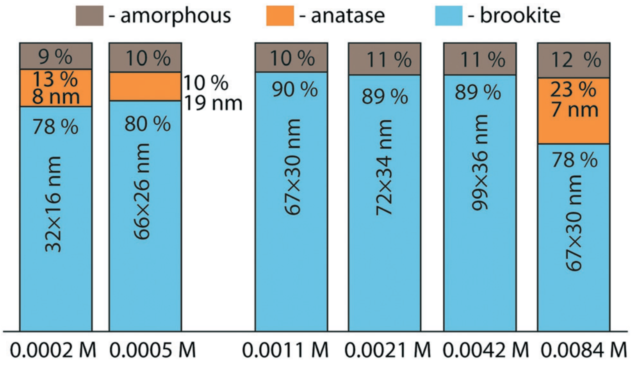


Fig. 8 Crystallite sizes and phase composition of the samples prepared by varying the concentration; the reaction temperature was 180 °C, time was 48 hours, titanium lactate (*C* = 0.0002–0.0084 M) was used as a precursor, pH 11.

product, and the attachment of anatase particles also becomes hindered. Thus, the crystallization of brookite does occur *via* oriented attachment of anatase and anatase-like particles with subsequent phase transition, while Ostwald ripening cannot be excluded.

Conclusions

Detailed analysis of the influence of synthetic conditions (temperature, time and precursor concentration) allowed us to establish the mechanism of brookite growth under hydrothermal conditions in an alkaline medium. Data obtained indicate that oriented attachment of anatase primary particles, which are formed by hydrolysis of the titanium lactate complex, is the key mechanism for brookite formation, while the Ostwald ripening mechanism cannot be completely excluded. Within the framework of the oriented attachment model, when anatase aggregates approach critical size, the phase transition into brookite occurs. This hypothesis agrees well with the thermodynamic data on the stability of TiO_2 polymorphs: anatase is the most stable phase only in the case of smaller particles (less than 17 nm in diameter). It was found that, at the initial stage, anatase and X-ray amorphous particles with an anatase-like structure are formed, but there are no brookite phase seeds of less than 10 nm. The size range of the thermodynamically stable brookite is 10–35 nm, and our observations agree with the thermodynamic model. The smallest crystallite size of brookite observed was 24 × 11 nm.

The suggested mechanism can be generalized to other cases in which different crystalline structures form under hydrothermal conditions: the synthesis of brookite and rutile from titanium complexes with other hydroxyl acids or inorganic ligands, synthesis of different polymorphs of MnO_2 and ZrO_2 under hydrothermal conditions, and many other systems. Moreover, a similar formation mechanism of brookite may take place under geological conditions.

The experiments reported in this paper made it possible to obtain exact information on the temperature, time and concentration ranges within which the pure brookite phase crystallizes. This will facilitate studies of the band structure, catalytic properties and other characteristics of this phase.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Russian Science Foundation (research project 17-73-10493). The facilities in the present work were used within the framework of the Program of the Development of Moscow State University.

References

1 A. Di Paola, M. Bellardita and L. Palmisano, *Catalysts*, 2013, **3**, 36–73.

2 M. Monai, T. Montini and P. Fornasiero, *Catalysts*, 2017, **7**, 304, DOI: 10.3390/catal7100304.

3 R. Kaplan, B. Erjavec, G. Drazic, J. Grdadolnik and A. Pintar, *Appl. Catal., B*, 2016, **181**, 465–474.

4 R. Verma, J. Gangwar and A. K. Srivastava, *RSC Adv.*, 2017, **7**, 44199–44224.

5 H. Zhang and J. F. Banfield, *J. Mater. Chem.*, 1998, **8**(9), 2073–2076.

6 C. Jia, X. Zhang and P. Yang, *Int. J. Hydrogen Energy*, 2018, **43**, 2237–2246.

7 P. K. Naicker, P. T. Cummings, H. Zhang and J. F. Banfield, *J. Phys. Chem. B*, 2005, **109**, 15243–15249.

8 M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, P. H. Borse, S. K. Kulkarni, G. S. Doran and H. J. Whitfield, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 6476–6481.

9 H. Zhang and J. Banfield, *J. Phys. Chem. B*, 2000, **104**(15), 3481–3487, DOI: 10.1021/jp000499j.

10 M. Kakihana, M. Kobayashi, K. Tomita and V. Petrykin, *Bull. Chem. Soc. Jpn.*, 2010, **83**(11), 1285–1308.

11 H. Kominami, Y. Ishii, M. Kohno, S. Konishi, Y. Kera and B. Ohtani, *Catal. Lett.*, 2003, **91**(1–2), 41–47.

12 T. A. Kandiel, A. Feldhoff, L. Robben, R. Dillert and D. W. Bahnemann, *Chem. Mater.*, 2010, **22**, 2050–2060.

13 T. A. Kandiel, L. Robben, A. Alkaim and D. Bahnemann, *Photochem. Photobiol. Sci.*, 2013, **12**, 602, DOI: 10.1039/c2pp25217a.

14 M. Kobayashi, H. Kato and M. Kakihana, *Nanomater. Nanotechnol.*, 2013, **3**(1), 1, DOI: 10.5772/57533.

15 M. Kobayashi, K. Tomita, V. Petrykin, M. Yoshimura and M. Kakihana, *J. Mater. Sci.*, 2008, **43**, 2158–2162.

16 K. Tomita, V. Petrykin, M. Kobayashi, M. Shiro, M. Yoshimura and M. Kakihana, *Angew. Chem., Int. Ed.*, 2006, **45**, 2378–2381.

17 Q. Duc Truong, L. X. Dien, Dai-Viet, N. Vo and T. S. Le, *J. Solid State Chem.*, 2017, **251**, 143–163.

18 O. Frank, M. Zukalova, B. Laskova, J. Kurti, J. Koltaib and L. Kavan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14567–14572.

19 C. Jia, X. Zhang, K. Matras-Postolek, B. Huang and P. Yang, *Carbon*, 2018, **139**, 415–426.

20 V. Petricek, M. Dusek and L. Palatinus, *Z. Kristallogr. - Cryst. Mater.*, 2014, **229**, 345–352.

21 A. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447–452.

22 V. A. Lebedev, D. A. Kozlov, I. V. Kolesnik, A. S. Poluboyarinov, W. Grünert and A. V. Garshev, *Appl. Catal., B*, 2016, **195**, 39–47.

23 I. V. Kolesnik, G. S. Chebotaeva, L. V. Yashina, E. A. Konstantinova, A. A. Eliseev, A. V. Lukashin and Y. D. Tretyakov, *Mendeleev Commun.*, 2013, **23**(1), 11–13.

24 J. Xu, K. Li, S. Wu, W. Shi and T. Peng, *J. Mater. Chem. A*, 2015, **3**, 7453–7462.

25 H. Zhang and J. F. Banfield, *Chem. Rev.*, 2014, **114**(19), 9613–9644.

26 R. Li, Y. Weng, X. Zhou, X. Wang, Y. Mi, R. Chong, H. Han and C. Li, *Energy Environ. Sci.*, 2015, **8**, 2377–2382.

27 Y. Xu, H. Lin, L. Li, X. Huang and G. Li, *J. Mater. Chem. A*, 2015, **3**, 22361, DOI: 10.1039/c5ta05953d.

28 M. Zhang, T. Chen and Y. Wang, *RSC Adv.*, 2017, **7**, 52755, DOI: 10.1039/c7ra11515f.

29 V. K. Ivanov, P. P. Fedorov, A. E. Baranchikov and V. V. Osiko, *Russ. Chem. Rev.*, 2014, **83**(12), 1204–1222.

30 H. Cölfen and M. Antonietti, *Mesocrystals and Nonclassical Crystallization*, Wiley, Chichester, England, 2008.

31 R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969–971.

32 R. L. Penn and J. F. Banfield, *Am. Mineral.*, 1998, **83**, 1077–1082.

33 I. A. Mudunkotuwa and V. H. Grassian, *J. Am. Chem. Soc.*, 2010, **132**, 14986–14994.

34 J. M. Pettibone, D. M. Cwiertny, M. Scherer and V. H. Grassian, *Langmuir*, 2008, **24**, 6659–6667.

35 R. L. Penn and J. F. Banfield, *Geochim. Cosmochim. Acta*, 1999, **63**(10), 1549–1557.

36 G. A. Seisenbaeva, G. Daniel, J.-M. Nedelec and V. G. Kessler, *Nanoscale*, 2013, **5**, 3330, DOI: 10.1039/c3nr34068f.

37 M. P. Finnegan, H. Zhang and J. F. Banfield, *Chem. Mater.*, 2008, **20**, 3443–3449.

38 I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids*, 1961, **19**, 35–50.

39 C. Wagner, *Z. Elektrochem.*, 1961, **65**, 581–591.

40 J. Schmidt and W. Vogelsberger, *J. Solution Chem.*, 2009, **38**, 1267–1282.