

MESOCRYSTAL SELF-ASSEMBLY OF
HIERARCHIC RUTILE-TYPE TiO₂
STRUCTURES

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Doctoral Dissertation
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Doctoral Dissertation

MEZOKRISTALNO SAMOUREJANJE HIERARHIČNIH
STRUKTUR NA OSNOVI RUTILNEGA-TIPA TiO_2

Doktorska disertacija

Supervisor: Prof. Dr. Aleksander Rečnik

Ljubljana, Slovenia, November 2018

*“I am just a child who has never grown up. I still keep asking these
'how' and 'why' questions. Occasionally, I find an answer.”*
- STEPHEN HAWKING -

To my Family.

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*“Feeling gratitude and not expressing it is
like wrapping a present and not giving it.”*
- WILLIAM ARTHUR WARD -

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Abstract

In the past few years, the growing need for renewable energy sources has driven a rapid development of new hierarchic materials, focusing on the production of complex 3D inorganic mesomaterials. Among numerous approaches proposed in the literature, self-assembly has recently become a very powerful method to create versatile nanostructured inorganic mesomaterials that challenge our conventional views of crystal growth by the attachment of fully grown nanocrystal units. Looking from an application point of view, recently published review pointed out:

*“What is needed are **fast** and **easily** controllable self-assembly **mechanisms**, which ideally work at **room temperature**.”*

(E. Sturm and H. Cölfen, 2017)

While diverse mesomaterials with promising properties have been synthesized with great success, proper understanding of the driving force of the mesocrystal assembly has not yet evolved. One of the main reasons is the lack of experimental evidence that would lead to a theoretical consensus on its nature.

In my thesis I address the problem of the self-assembly mechanism, which was exploited to the extent of full control over final rutile's TiO_2 3D branched morphology. The first part of the thesis deals with multilevel branched structures produced by the self-assembly of primary rutile precipitates and uncovers the key processes controlling this non-classical crystallization path. I have shown that the formation of complex mesocrystals of rutile is accomplished by the oriented attachment of nanocrystalline precipitates along low-energy planes, resulting in lateral attachment and twinning. Moreover, the first experimental evidence that indicates the presence of electromagnetic force-fields being active during oriented attachment of nanocrystals is provided. In the second part, the two identified self-assembling modes of rutile, together with variation in supersaturation were exploited in order to get the control over oriented attachment and twinning. The results showed the dependence of twin incidents on aspect ratio of precipitated rutile nanocrystals, which is linearly increasing with medium acidity, *i.e.* the lower it is, the higher the affinity for twin oriented attachment. To quantify the degree of branching of rutile mesocrystals, we proposed a new generally applicable criterion, the so-called morphology factor. It provides a quantitative measure of nanoparticle morphology and can be used to evaluate the increase of specific surface area for any material, independently of their size. Finally, in the last part, all the knowledge on the self-assembly mechanism was used and focused on the production of applicable, *i.e.* homogeneous and reproducible twin-based rutile mesocrystals. We achieved homogeneous branched products by the low-temperature synthesis strategy that is based on continuous homogenization of the reactive solution. The results showed the importance and impact of homogeneity on the specific surface area of the mesocrystals, expressed in terms of morphology factor, and approaches the above target.

Povzetek

V zadnjih letih je pomanjkanje obnovljivih virov energije spodbudilo hiter razvoj novih hierarhičnih materialov, s posebnim poudarkom na kompleksnih 3D anorganskih mezokristalih. Med številnimi pristopi, predlaganimi v literaturi, pa je samourejanje v zadnjem času postala vodilna metoda za izdelavo vsestranskih nanostrukturnih anorganskih mezomaterialov, ki preizkušajo naše znanje o konvencionalni rasti kristalov z usmerjenim urejanjem nanokristalnih gradnikov. Nedavno objavljen literaturni pregled je, gledano z aplikativnega vidika, izpostavil sledečo problematiko:

*“Nujni so **hitro in enostavno** obvladljivi **mehanizmi** samourejanja, ki, idealno gledano, delujejo pri **sobni temperaturi**.”*

(E. Sturm in H. Cölfen, 2017)

Medtem ko raznovrstni mezomateriali z obetavnimi lastnostmi že obstajajo, pa se razumevanje gonilne sile, ki vodi v njihov nastanek, še vedno ni razvilo. Eden od glavnih razlogov za to je pomanjkanje eksperimentalnih dokazov, ki bi privedli do teoretičnega soglasja glede njihove narave.

V doktorskem delu rešujem problematiko mehanizma samourejanja z namenom pridobiti popolno kontrolo nad končno, 3D razvejano morfologijo rutila TiO_2 . Prvi del doktorskega dela obravnava v več ravneh razvejane strukture, ki nastanejo z mehanizmom samourejanja primarnih rutilnih precipitativ in razkriva ključne procese, ki nadzorujejo to neklasično kristalizacijsko pot. Pokazala sem, da kompleksni mezokristali rutila nastanejo z usmerjenim urejanjem nanokristaliničnih precipitativ vzdolž nizkoenergijskih ravnin, kar lahko vodi bodisi v bočno ali bodisi dvojčno urejanje. Poleg omenjenega pa doktorsko delo prikazuje tudi prvi eksperimentalni dokaz o prisotnosti aktivnih elektromagnetnih sil med usmerjenim urejanjem nanokristalov. Cilj drugega dela raziskav je popoln nadzor nad identificiranim mehanizmom samourejanja, *tj.* usmerjeno ureditvijo precipitativ, ter dvojčenjem v kombinaciji z variacijo prenasajenja. Rezultati kažejo odvisnost nastanka dvojčkov od razmerja stranic precipitiranih rutilnih nanokristalov, ki linearno narašča s kislostjo medija, *tj.* nižja kot je kislost, večja je verjetnost za nastanek dvojčka. Da bi lahko ovrednotili razvejane mezokristale rutila, je v tem doktorskem delu predlagan tudi *t. i.* morfološki faktor kot kvantitativno merilo za različne nanokristalne morfologije, uporaben za ovrednotenje povečanja specifične površine za kateri koli material ne glede na velikost. V zadnjem delu je pridobljeno znanje o mehanizmu samourejanja usmerjeno v nastanek uporabnih, *tj.* ponovljivih in homogeno razvejanih rutilnih mezokristalov. Njihov nastanek smo omogočili z nizko-temperaturno sintezo, ki temelji na kontinuirani homogenizaciji reakcijske raztopine. Rezultati, izraženi z novo vpeljanim morfološkim faktorjem, kažejo vpliv in pomen homogenosti na specifično površino mezokristalov in se približajo zgoraj zastavljenemu cilju.

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Appendix A. Self-Assembly of Multilevel Branched Rutile-Type TiO₂ Structures Via Oriented Lateral and Twin Attachment: *Article's Supporting Information*

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Abbreviations

A	... Anatase
AFM	... Atomic force microscopy
BET	... Brunauer-Emmett-Teller
compl. int.	... Complementary interface
cos	... Trigonometric cosine function
c-rut	... Rutile crystals from Cinkarna Celje, Slovenia
CSD	... Chemical solution deposition
CVD	... Chemical vapor deposition
DLS	... Dynamic light scattering
ECS	... Equilibrium crystal shape
ED	... Electrodeposition
EDP	... Electron diffraction pattern
EDS	... Energy dispersive X-ray spectroscopy
<i>eg.</i>	... Exempli gratia – for example
<i>et al.</i>	... Et alii – and others
<i>etc.</i>	... Et cetera – and other similar things
ETEM-AFM	... Environmental transmission electron microscopy-atomic force microscopy
FEG-SEM	... Field emission gun-scanning electron microscopy
FFT	... Fast fourier transform
HRTEM	... High resolution transmission electron microscopy
HT	... Hydrothermal
<i>i.e.</i>	... Id est – that is
L	... Liquid
MD	... Molecular dynamics
m-rut	... Mesocrystalline rutile
N	... Nucleus
n.a.	... Not applicable
OA	... Oriented attachment
PDI	... Polydispersity index
pH	... Measure of basicity or acidity
PVD	... Physical vapor deposition
p.z.c.	... Point of zero charge
R	... Rutile
RT	... Room temperature
S	... Substrate
SAED	... Selected area electron diffraction
s-rut	... Seed rutile crystals
SSA	... Specific surface area

ST	... Solvothermal
TEM	... Transmission electron microscopy
<i>t. i.</i>	... Tako imenovani
TiO ₂ (II), TiO ₂ (III),	... Polymorphs of TiO ₂
TiO ₂ (B), TiO ₂ (H),	
TiO ₂ (R), TiO ₂ (OI),	
TiO ₂ (OII)	
Ti(IV)-butoxide	... Titanium(IV) butoxide = Ti(OC ₄ H ₉) ₄
<i>tj.</i>	... To je
TMS	... Tetramethylsilane = Si(CH ₃) ₄
UV	... Ultraviolet
vdW	... van der Waals
VLS	... Vapor liquid solid
XRD	... X-ray powder diffraction
1D	... One-dimensional
2D	... Two-dimensional
3D	... Three-dimensional
¹ H-NMR	... Proton nuclear magnetic resonance
1 st gen.	... First generation
2 nd gen.	... Second generation

Symbols

a	... Unit cell parameter
A	... Surface area of a particle
A'	... Calculated surface area of a particle
A_0	... Surface area of a sphere
A_0'	... Calculated surface area of a sphere
b	... Unit cell parameter
c	... Solute concentration or unit cell parameter
c_{HCl}	... Concentration of HCl
c_{max}	... Maximum solute's concentration in solution
c_{min}	... Minimum solute's concentration in solution needed to start the nucleation
c_o	... Equilibrium concentration of solute in solution
c_s	... Concentration of a solute in a solid phase
c_{ss}	... Concentration of a solute in a supersaturated solution
$c[\text{H}^+]$, $c[\text{H}_3\text{O}^+]$	... Molar concentration of acid
$c[\text{OH}^-]$	... Molar concentration of hydroxide ions
d	... Distances between crystallographic planes
D	... Distance between two surfaces
D_0	... Effective hydrodynamic diameter
D_0'	... Calculated effective hydrodynamic diameter
E	... Surface potential
F	... Coulombic force
F_c	... Faraday's constant = $9.650 \cdot 10^4 \text{ Cmol}^{-1}$
$f(\theta)$	... Wetting factor
hkl	... Miller indices
i	... new generation of crystals
$I4_1/\text{amd}$	... Body-centered tetragonal space group
k	... Boltzmann constant = $1.381 \cdot 10^{-23} \text{ JK}^{-1}$
k_e	... Coulomb's constant = $8.990 \cdot 10^9 \text{ Nm}^2\text{C}^{-2}$
$K_{\text{H}_2\text{O}}$	... Water's dissociation constant = 10^{-14}
l/w	... <i>Length</i> (along c-axis)/ <i>width</i> (of {110} prisms) = aspect ratio
m	... Mass of a sphere
M	... Metal atom
n	... Oxidation state of M
N	... Total number of crystals
OR	... Alkoxide group
Pbca	... Primitive orthorhombic space group

$P4_2/mnm$	... Primitive tetragonal space group
q_1, q_2	... Charge magnitudes of approaching species
ROH	... Alcohol
r	... Nuclei/particle radius
R	... Alkyl group
R_g	... Gas constant = $8.314 \text{ JK}^{-1}\text{mol}^{-1}$
r_s	... Distance between approaching species
r^*	... Critical nuclei radius
S	... SSA of a particle
S'	... Calculated SSA of a particle
S_0	... SSA of a sphere
S_0'	... Calculated SSA of a sphere
T	... Temperature
T_E	... Equilibrium temperature
V	... Volume of a particle
V'	... Calculated volume of a particle
V_0	... Volume of a sphere
()	... Planes of crystal structures and their correct repetitions at certain distances
2Θ	... Angle between transmitted and reflected X-ray beam
< >	... Family of crystal directions
ΔG	... Total Gibbs free energy
ΔG_V	... Change of Gibbs free energy per unit volume
ΔG^*	... Critical Gibbs free energy
$\Delta G_{\text{hetero}}^*$	... Critical Gibbs free energy at heterogeneous nucleation
ΔG_{homo}^*	... Critical Gibbs free energy at homogeneous nucleation
$\Delta \mu_S$	... Change of surface free energy of a spherical nucleus
$\Delta \mu_V$	... Change of volume free energy of a spherical nucleus
Σ	... Sum
Ω	... Atomic volume
Ψ	... Sphericity
Ψ'	... Calculated sphericity
[]	... Crystallographic directions = vector connecting the coordinate origin and a certain point of a unit cell
δ	... Partial charges or chemical shift in ^1H -NMR analysis
γ	... Surface energy per unit area
γ_{LN}	... Gibbs free energy for liquid-nucleus surface area
γ_{NS}	... Gibbs free energy for nucleus-substrate surface area
γ_{SL}	... Gibbs free energy for substrate-liquid surface area
π	... Pi = 3.142
θ	... Contact angle
ρ	... Density of a particle
$\rho_m(\infty)$	... Bulk liquid density
$\rho_m(D)$	... Contact liquid density
$\rho_s(D)$	... Midplane liquid density
{ }	... Family of crystal planes
f_m	... Morphology factor

f_{m}' . . . Calculated morphology factor

Chemical Symbols

Ag	... Silver
Al	... Aluminum
AlN	... Aluminum nitride
Al ₂ O ₃	... Aluminum oxide
Au	... Gold
BaCO ₃	... Barium carbonate
BaCrO ₄	... Barium chromate
BaTiO ₃	... Barium titanate
CaCO ₃	... Calcium carbonate
CdS	... Cadmium sulfide
Ce	... Cerium
CeO ₂	... Cerium(IV) oxide
Cl ⁻	... Chloride ion
Co ₃ O ₄	... Cobalt(II,III) oxide
Cu	... Copper
Cu ₂ O	... Copper(I) oxide
C ₂ H ₄ O ₃	... Glycolic acid
C ₂ H ₄ (OH) ₂	... Ethylene glycol
C ₄ H ₉	... Alkyl group
C ₄ H ₉ OH	... n-butanol
D ₂ O	... Deuterium oxide = heavy water
Fe	... Iron
Fe ³⁺	... Iron ion
Fe ₂ O ₃	... Iron(III) oxide
Fe ₃ O ₄	... Iron(II, III) oxide
FePt	... Iron platinum
FeSi	... Iron silicide
GaN	... Gallium nitride
GaP	... Gallium phosphide
GaSb	... Gallium antimony
H	... Hydrogen
H ⁺	... Hydrogen ion
HCl	... Hydrochloric acid
HNO ₃	... Nitric acid
H ₂ O	... Water
H ₂ O ₂	... Hydrogen peroxide
H ₃ O ⁺	... Hydronium ion
K ₂ Ti ₆ O ₁₃	... Potassium hexatitanate
Li ₂ FeSiO ₄	... Lithium iron silicate
MnO ₂	... Manganese(IV) oxide

MnOOH	... Manganese oxide hydroxide
Mn _x Fe _{1-x} O	... Iron-manganese oxide
Na ⁺	... Sodium ion
NaCl	... Sodium chloride
NH ₃	... Ammonia
N ₂	... Nitrogen gas
O	... Oxygen
OC ₄ H ₉	... Alkoxide group
OH ⁻	... Hydroxide ion
PbCl ₂	... Lead(II) chloride
PbS	... Lead(II) sulfide
PbSe	... Lead(II) selenide
PbTiO ₃	... Lead(II) titanate
Pd	... Palladium
Pt ₃ Fe	... Isoferroplatinum
Sb ₂ O ₃	... Antimony(III) oxide
Si	... Silicon
SiO ₂	... Silicon(IV) oxide
SnO ₂	... Tin(IV) oxide
SrTiO ₃	... Strontium titanate
Ti	... Titanium
Ti ⁴⁺	... Titanium ion
TiCl ₄	... Titanium(IV) chloride
TiO ₂	... Titanium(IV) oxide
Ti(OBu) ₄ = Ti(OC ₄ H ₉) ₄	... Titanium(IV) butoxide
Ti(OH) ₄	... Titanium hydroxide
[Ti(OH) _{4-n} (OH ₂) _{2+n}] ⁿ⁺ _{n=1,2,3}	... Titanium-hydroxo-aquo complex
Ti(OiPr) ₄	... Titanium(IV) isopropoxide
TiO ₆	... Titanium octahedron
VO ₂	... Vanadium(IV) oxide
V ₂ O ₅	... Vanadium(V) oxide
ZnO	... Zinc oxide
Zn ₃ P ₂	... Zinc phosphide
Zn ₂ TiO ₄	... Zinc titanate
α-PbO ₂	... Alpha-type Lead(IV) oxide
γ-MnO ₂	... Gamma-type Manganese(IV) oxide

Glossary

Anisotropy – property of a material with different physical or mechanical properties along specific crystallographic direction

Birefringence – property of a material with a refractive index depending on the propagation direction and polarization of light

Catalyst – a substance that alters and accelerates chemical reaction rates

Centrosymmetry – a point through which a crystal displays inversion symmetry, *i.e.* for every atom at (x,y,z) position relative to the center of symmetry in the unit cell there is an atom at (-x, -y, -z) positions

Coordination number – the number of species bound to a certain atom

Dehydration reaction – chemical reaction accompanied by the loss of water molecule from the reacting species

Deprotonation – transfer or removal of a proton from species, forming a conjugate base

Dissociation – splitting of molecules/complexes into smaller species, *i.e.* atoms, ions or radicals

Effective hydrodynamic diameter – diameter of a spherical particle that diffuses at the same speed as the particle that is being measured

Fractal – complex, usually branched, self-similar crystal across different scales, which is created by a fast, diffusion-limited repeating process

Friedelian twin – twinned crystal with matching crystal lattices of participating crystals

Hybrid twin – twinned crystal that does not have straightforward matching crystal lattices of participating crystals, instead they may only exhibit matching two or more sublattices

Hybridization – a concept of combining atomic orbitals into hybrid orbitals, for subsequent formation of new covalent bonds

Intramolecular proton transfer – a process by which an “excess” proton is jumping from one molecule/complex to another by forming a new covalent bond

Isometry – property of a material with identical physical or mechanical properties along all crystallographic directions

Protic solvent – solvent that contains a labile hydrogen atom

Polycondensate – a substance that is formed by condensation reactions

Polydispersity index – dimensionless measure of the size distribution's curve broadness (sample's non-uniformity), *i.e.* number higher than 0.7 indicates a very broad particle's size distribution

Protonation – transfer or addition of a proton to species, forming a conjugate acid

Thermal agitation – increase in temperature

Topotaxial reaction – a solid-state reaction in which a crystalline precursor determines the orientation of the final product

Chapter 1

Introduction

The first Chapter provides an in-depth literature overview and introduction to mesocrystalline materials linked to their unique, non-classical growth mechanisms based on self-assembly. The focus is set on the synthesis, understanding and origin of branched mesomaterials.

1.1 Mesocrystals

Mesocrystals were first introduced by Cölfen and Antonietti in 2005 [1]. The word mesocrystal stands for a mesoscopically structured crystal that represents a hierarchical superstructure composed of individual primary nanocrystals self-assembled in a common crystallographic fashion. Since then, mesocrystals are understood as architectures with well-defined facets and long-range ordering on the atomic scale, which can transform into single crystals by fusion of nanoparticles (Figure 1.1) [2]. Mesocrystals are produced by *self-assembly* of nanocrystalline building blocks that challenge our conventional views of crystal growth by simple attachment of atoms. This non-classical growth is defined as a process by which primary nanocrystals self-organize into mesostructures with a high degree of crystallographic registry between the individual subunits. It happens spontaneously, due to specific non-covalent interactions and without external guidance.

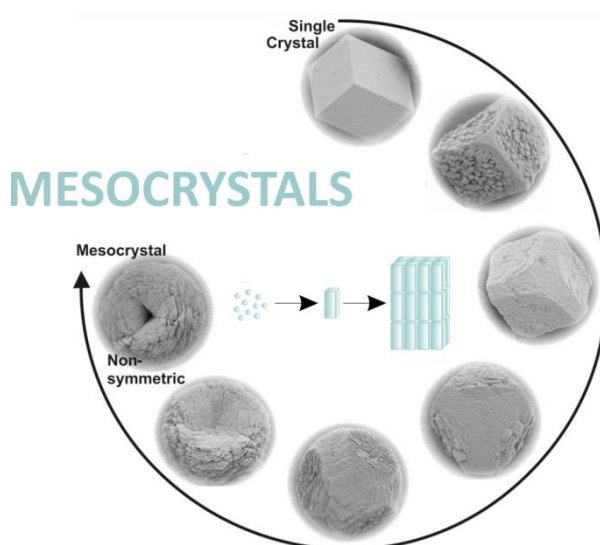


Figure 1.1: Morphological interplay between meso- and single crystals of rhombohedral CaCO_3 , showing different degrees of mesocrystallinity. Adapted from Cölfen and Antonietti [1].

Although mesocrystalline materials were introduced to a wide scientific community already about 15 years ago, they are not a recent discovery. The first experimental indication of crystal assemblies in synthetic materials dates back to 1925, when Blüh [3] observed organized aggregation of rod-like V_2O_5 particles on a glass surface that were, due to limited analytical possibilities at that time, not appropriately characterized [3]. Later, Distler and Borisova (1967) [4] reported on the assemblies of PbSe particles oriented in close-packed monolayers with their $\{111\}$ faces parallel to the silicon substrate, whereas one of the earliest real evidences of self-assembly and existence of mesocrystals was given by Frondel (1978) [5] who studied the origin of natural twisted (gwindel) quartz (SiO_2) crystals. He suggested the origin of twisting is in the assembly of quartz fibers that are twisted due to piezoelectric polarization during their growth in hydrothermal (HT) solutions, possibly indicating their mesocrystalline origin. The existence of mesocrystals was further confirmed by Matijević *et al.* (1988) [6] with the synthetic study of various Ce^{IV} compounds. He showed that plate-like nanoparticles self-aligned and gave rise to mesocrystalline superstructures. Later studies confirmed the observations in these early reports and revealed that the symmetry-related angular dispersion of individual building blocks in mesocrystalline quartz is not an isolated example of this phenomenon. Cölfen and Antonietti (2005) [1] have shown a beautiful example of rhombohedral twisting of calcite ($CaCO_3$) that is also commonly observed in rhombohedral carbonates that crystallize from HT solutions in nature. Other examples of symmetry-related twisting include fluorapatite [7], ZnO [8]–[13], AlN [14], GaN [15], *etc.* [16], [17]. Common to these studies is that the crystals display angular twists following symmetry-specific rules, and the existence of twisting appears to be the most reliable macroscopic evidence of mesocrystal assembly. Today, numerous materials have been recognized to exhibit self-assembly necessary to grow versatile mesocrystals, and can be categorized according to their chemical composition as represented in Table 1.1. Their assembly is achieved by using versatile techniques, such as evaporation-mediated and template-assisted methods, gas phase diffusion and Langmuir-Blodgett film deposition techniques, external field directed self-assembly, *etc.* [18], [19] on substrates or directly in reactive solution.

Table 1.1: Typical self-assembling materials, categorized according to their chemical compositions.

Typical self-assembling materials		
metals	metal oxides	complex compounds
Pd [20], Cu [21], Au [22], [23], Ag [24], <i>etc.</i> [25], [26]	SnO_2 [27], [28], ZnO [8], [29], [30], TiO_2 [31]–[37], Fe_2O_3 [38]–[40], Fe_3O_4 [41], Cu_2O [42], CeO_2 [43], Co_3O_4 [44], VO_2 [45], MnO_2 [46], Sb_2O_3 [47], <i>etc.</i> [2]	PbS [48], [49], PbSe [50], [51], hydroxyapatite [52], [53], CdS [54]–[56], $CaCO_3$ [57], $SrTiO_3$ [58], $BaCO_3$ [59], $BaCrO_4$ [60], $BaTiO_3$ [61], <i>etc.</i> [2]

As shown in Table 1.1, there is virtually no material that would be unsuitable for growing mesocrystalline structures *via* one- (1D), two- (2D) or three-dimensional (3D) self-assembly (Figure 1.2) [1]. Regardless of their versatile dimensionality, it still remains a challenge to transfer them into industrial applications, mainly because their growth mechanisms are not understood. Understanding their formation mechanisms is essential in order to control the experimental outcome upon changes of experimental conditions, not only for fundamental science but also in the field of scaled-up applications. Nevertheless, owing to their structural and morphological versatility, as well as their unique properties arising from the individual nano building units, mesocrystals have

already shown unprecedented performance in laboratory-scale photocatalysis [42], [62], electrode and optoelectronic materials [63]–[65], as well as in adsorption [66], [67], highly selective biomolecular separation processes [68], [69], *etc.* [70], [71].

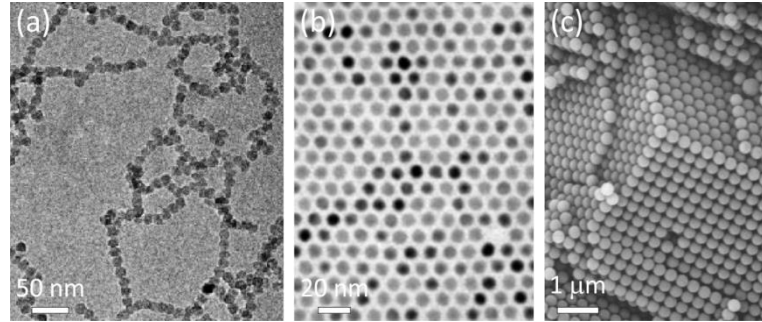


Figure 1.2: Examples of (a) 1D assembly of SiO₂ nanospheres [72], (b) 2D assembly of PbSe nanocrystals [73] and (c) 3D assembly of colloidal polystyrene nanoparticles [74].

1.2 Self-Assembly

Ever since 1998, when Penn and Banfield [36] reported on oriented attachment (OA) of anatase TiO₂ nanocrystals, self-assembly by OA has slowly started to change our conventional understanding of crystal growth. Owing to its overall complexity, self-assembly is still not completely understood, however there have emerged some inevitable facts showing how classical crystal growth differentiates from non-classical mesocrystal growth. They are highlighted in the following subchapters.

1.2.1 Nucleation and classical growth of crystals

Nucleation is a sequence of atomic or molecular processes by which growth units of a reactant phase arrange into a nanocrystal large enough to have the ability to irreversibly grow to a macroscopically larger crystal. It is the process of generating a new phase from a precursor whose free energy has become higher than that of the emerging new phase and it starts *via* the formation of small embryos of the new phase inside the large volume of the old phase [75], [76]. Nucleation can be divided into two modes, *i.e.* homogeneous and heterogeneous nucleation, described in detail in the next subchapters [77].

1.2.1.1 Homogeneous nucleation

By homogeneous nucleation, nanoparticles can be synthesized in three media, *i.e.* liquid, gas and solid. The fundamentals of nucleation and subsequent crystal growth are principally the same and will be described hereinafter.

Homogeneous nucleation can be kinetically or thermodynamically controlled. The first is produced by limiting the space (micelle or aerosol syntheses) or amount of the precursor available for growth, whereas thermodynamically controlled crystallization consists of the formation of supersaturation, followed by nucleation and subsequent growth of a crystal by orderly addition of the growth units (atom, ion or molecule). Supersaturation can be achieved by changing the temperature, pH, pressure or by the evaporation of solvent in order to decrease the volume of saturated solution [77], [78]. The driving force for both nucleation and subsequent growth of particles is the total Gibbs free energy (ΔG). Figure 1.3 shows an example of homogeneous nucleation of a solid phase from a supersaturated solution. A solute in a supersaturated solution with concentration exceeding the supersaturation, c_{ss} , possesses a high Gibbs free energy and

in order to reduce it, it precipitates from the solution as a solid product with concentration c_s . As a result the concentration of the solute in the solution decreases to lower equilibrium concentration, c_o [77].

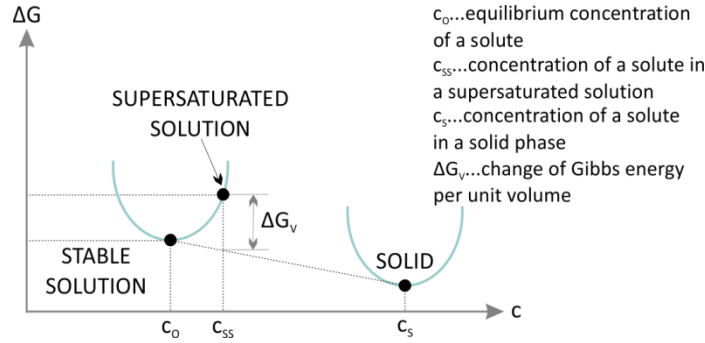


Figure 1.3: Schematic reduction of the total Gibbs free energy (ΔG) of a supersaturated solution by forming a solid phase and maintaining an equilibrium concentration in the solution [77].

The reduction of ΔG sets off the nucleation and the subsequent growth of the crystal from the nuclei if the amount of energy is sufficient. The change of Gibbs free energy per unit volume ΔG_v of the solid phase forming from the solution is defined as:

$$\Delta G_v = - \frac{kT}{\Omega} \ln\left(\frac{c}{c_o}\right) \quad (1.1)$$

where k is the Boltzmann constant, T is the temperature, Ω is the atomic volume, c is the solute concentration and c_o the equilibrium concentration [77], [78]. When $c = c_o$, ΔG_v is zero, then no supersaturation is present. Consequently no nucleation would occur, however when $c > c_o$, ΔG_v becomes negative (Eq. 1.1) and nucleation occurs spontaneously. For spherical nucleus with radius r , nucleation causes the change of Gibbs free energy or volume energy, $\Delta \mu_v$ and introduces a new surface in the system, which results in the increase of the surface energy, $\Delta \mu_s$. Total Gibbs free energy, ΔG is a sum of both. The total Gibbs free energy or the total change of chemical potential for the formation of the nucleus is given by the sum of volume energy and surface energy, which is a result of the formation of a new phase. Total Gibbs free energy for spherical nuclei is then defined as [77]:

$$\Delta G = \Delta \mu_v + \Delta \mu_s = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (1.2)$$

where γ is the surface energy per unit area. As it can be seen in Figure 1.4, nucleation of the solid phase from a supersaturated solution can start when the nucleus is large enough and it can only be stable when its radius exceeds the critical radius, r^* . When critical nuclei size is reached, critical free energy, ΔG^* needed for nucleation is exceeded, leading to the decrease of the total Gibbs energy of the system [77], [78].

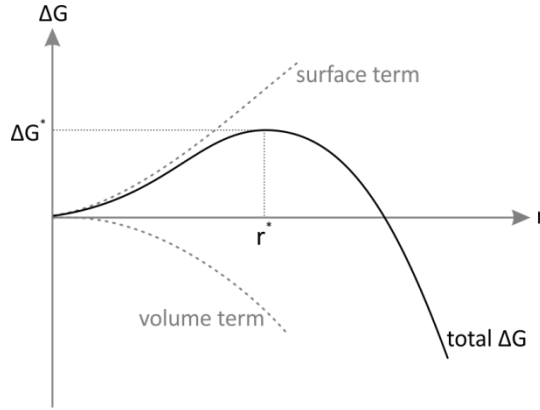


Figure 1.4: The change of volume energy ($\Delta\mu_v$), surface energy ($\Delta\mu_s$) and total free energy (ΔG) as a function of spherical nucleus radius [77], [78].

Critical radius thus represents the minimum size of a stable spherical nucleus. If a nucleus is smaller than the critical radius, it will dissolve back into the solution and reduce the total free energy. On the other hand, if the nucleus is larger than the critical radius, it is stable and it can grow further into a larger crystal. Critical spherical radius r^* needed for nucleation is defined by [77]:

$$r^* = -2 \frac{\gamma}{\Delta G_v} \quad (1.3)$$

and accompanied by critical free energy (ΔG^*):

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2} \quad (1.4)$$

that needs to be exceeded in order for the nucleation to start [77], [78].

The most important parameter that influences the critical free energy and critical nuclei radii is temperature. A comparison between the critical free energy and critical radius for a spherical nucleus with different supersaturation degrees is shown in Figure 1.5.

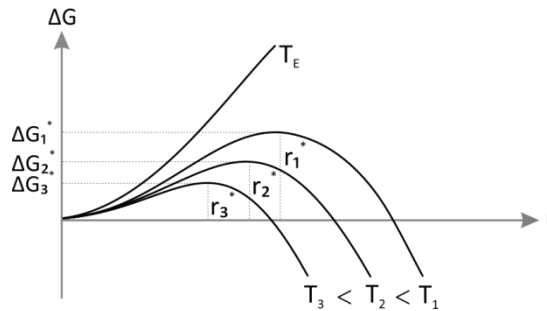


Figure 1.5: The effect of temperature on the critical free energy and nucleus sizes with different degrees of supersaturation. Supersaturation increases with decreasing temperature, whereas free energy decreases with decreasing temperature. Temperatures are lower than equilibrium temperature (T_E) and follow $T_3 < T_2 < T_1$ [77].

Supersaturation decreases with an increasing temperature, *i.e.* lower energy needs to be overcome for nucleation at a lower temperature. At a high temperature, larger nuclei are formed than at a low temperature. At the diagram it is seen that high

supersaturation and low critical free energy result in nuclei with smaller radii. Changing the solvent, present additives or impurities influence the total free energy and consequently the critical radii of precipitated nuclei. In addition, the initial concentration of solute also influences the size of the nuclei. A low number of nuclei is also formed from solution with high viscosity, on the other hand low viscosity accelerates crystal growth [77].

Figure 1.6 shows LaMer's diagram [79], representing nucleation and classical growth of nuclei as a function of concentration and time. When the concentration of the solute increases with time, it eventually reaches its maximum point, whereas after that the concentration decreases due to the precipitation of nuclei and their subsequent growth. To start the nucleation, equilibrium concentration (c_o) is not enough and higher concentration of solute in the solution is needed, to exceed the critical free energy ΔG^* (Eq. 1.4). Only when the concentration of a solute in the solution reaches a minimum value (c_{min}) needed to overcome ΔG^* , nucleation can start. This regime in Figure 1.6 is represented by the range II. When a nucleation process starts, concentration and Gibbs free energy decrease due to nucleation at the initial stage and soon later due to crystal growth. Nucleus above its critical radius (r^*) starts to grow as soon as it is formed, therefore nucleation and growth are basically inseparable processes that proceed at different speeds. Growth of already formed nucleus will proceed until the concentration of solute reaches c_o [77]. To produce nuclei with uniform sizes, synthesis times need to be short, because nuclei produced at the same time have consequently the same time for subsequent growth. In addition, in order to achieve the size of nuclei as uniform as possible the concentration of solute needs to be increased rapidly to the saturation value and then quickly decreased below the minimum concentration (c_{min}). While c_{min} is the concentration needed for nucleation process, the growth process can take place all the way down to equilibrium concentration (c_o).

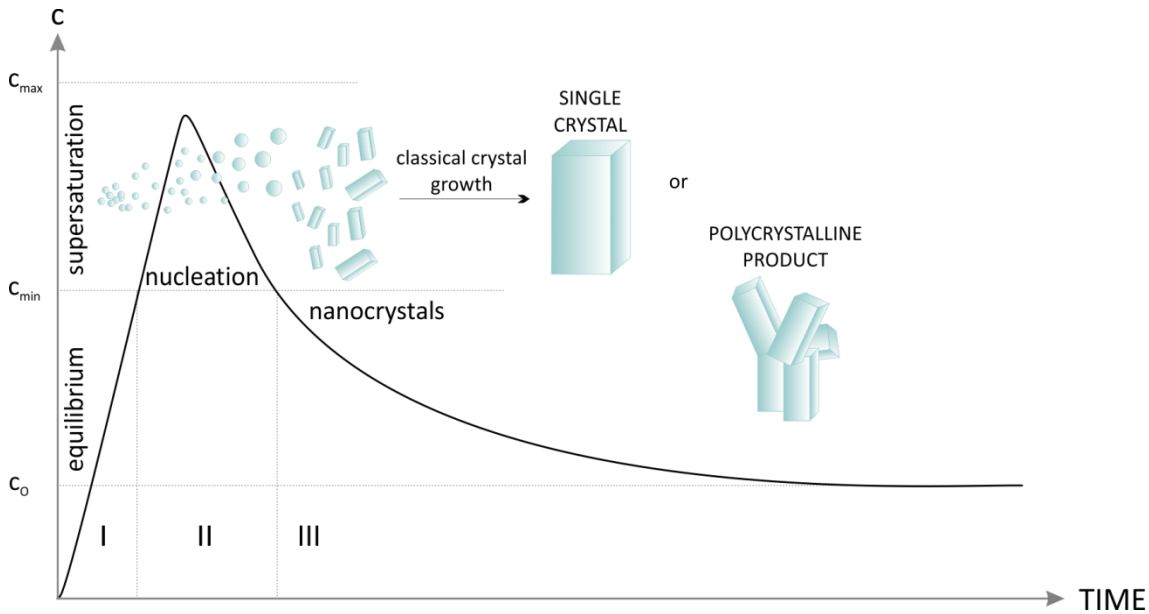


Figure 1.6: LaMer's model of nucleation and subsequent classical growth of nuclei into a single- or polycrystalline product as a function of solute concentration and time [79].

Kinetics of the subsequent growth defines the particle size distribution. Regardless of the distribution of nuclei, final particles have different sizes. Particle size distribution depends on how the growth process is controlled. It can be diffusion controlled, *i.e.*

controlled by the diffusion of growth units from the media to the nucleus surface, or growth controlled, *i.e.* controlled by the incorporation of growth units that are already on the nucleus surface. In the first case, the growth rate is controlled by diffusion of growth units from the solution onto the surface of the nucleus. If the growth rate is slow enough (slow diffusion), it results in monodispersed (equal size) crystallites. At this point growth units are formed with a slow chemical reaction or in a very viscous solution. However, the diffusion is considered fast when the concentration of growth units is the same in the bulk solution and on the surface of the nucleus. In this case, crystal growth is no more diffusion controlled, instead it is growth controlled. There are two possible mechanisms for the growth controlled process. The first is mononuclear growth, which occurs when the crystal is growing layer by layer and the next layer starts to grow when the previous is completed. Longer growing times result in crystals with a different radius, *i.e.* final powder is not monodispersed. The second is polynuclear growth, which occurs when the surface process is so fast that the next layer starts to grow before the previous one is completed. With time, the crystals grow to reduce radius difference which results in the formation of monosized crystallites [77].

Classical crystal growth leads to the emergence of single- or polycrystalline form of crystals (Figure 1.6). Most of the substances that we are dealing with are found in polycrystalline form, as it is very difficult to sustain stable conditions in the solution at which only one large enough crystal would appear at one place and grow further by the classical crystal growth. Nevertheless, some single crystals like quartz are produced by a controlled Ostwald ripening process, where smaller unstable crystals dissolve back into the solution and redeposit onto larger crystals [77]. However, in many cases the solution is usually not that stable and numerous smaller crystals in different sizes appear at different locations in the solution. These nanocrystals are highly unstable due to high surface/volume ratio and rather uncontrollably aggregate to relieve the high surface energy, which results in a polycrystalline product without any specific orientation between the nanocrystals [2].

1.2.1.2 Heterogeneous nucleation

Heterogeneous nucleation is a crystallization process that takes place on some sort of a substrate. It starts spontaneously and is much more common than homogeneous nucleation. It can start at phase boundaries, on impurities like dust particles, or when the seed layer of the same substance is predeposited on the surface. Consequently, because we already have a nucleation point that enables crystal growth, less energy is required than for homogeneous nucleation. For growth similar nonequilibrium conditions, like in homogenous nucleation, need to be established [77], [80].

The main difference between heterogeneous and homogeneous nucleation is in the fact that at heterogeneous nucleation growth units impinge onto the substrate and form a cap-shaped nucleus directly on its surface (Figure 1.7), whereas in homogeneous nucleation, particles are first formed in the growth medium and then deposited onto the substrate [77], [80].

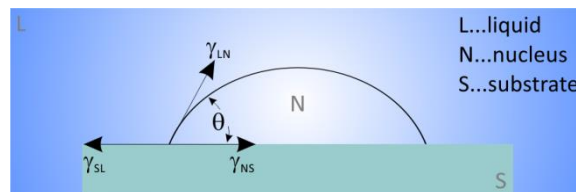


Figure 1.7: Process responsible for heterogeneous nucleation, representing a cap-shaped nucleus with all related interface energies in equilibrium [80].

Similar to homogeneous nucleation, Gibbs free energy decreases and surface energy increases when the nucleus is formed. The difference is that in heterogeneous nucleation surface energy consists of three interface energies: liquid-nucleus (γ_{LN}), nucleus-substrate (γ_{NS}) and substrate-liquid (γ_{SL}). For a planar solid surface on which heterogeneous nucleation is taking place, the equation that joins all three energies is defined by:

$$\gamma_{SL} = \gamma_{NS} + \gamma_{LN}\cos\theta \quad (1.5)$$

where θ is the contact angle which depends only on the surface properties or interfaces involved and it tells us how a new phase wets a solid substrate [77]. The critical free energy that the system needs to overcome for heterogeneous nucleation ($\Delta G^*_{\text{hetero}}$) is defined as a product of critical free energy needed for homogeneous nucleation (ΔG^*_{homo}) and a wetting factor ($f(\theta)$) [77]:

$$\Delta G^*_{\text{hetero}} = \Delta G^*_{\text{homo}} \cdot f(\theta) \quad (1.6)$$

The wetting factor depends on the contact angle between the nucleus and the surface [77]:

$$f(\theta) = \frac{(2-3\cos\theta + \cos^3\theta)}{4} \quad (1.7)$$

Wetting factor can have a value between 0 and 1. When the contact angle is 180° , the wetting factor equals 1, *i.e.* the critical energy barrier becomes the same as that of homogeneous nucleation, and the substrate has no influence on its nucleation. On the other hand when the contact angle is less than 180° , the energy barrier for heterogeneous nucleation is smaller than that of homogeneous nucleation (Figure 1.8) and the substrate present in the system promotes its nucleation. However, if the contact angle is 0° , the wetting factor is also zero and there is no energy barrier for the formation of a new phase. Such nucleation conditions are achieved by deposition on the surface of the same material. So, heterogeneous nucleation is easier, less energy is needed for it and it is observed as soon as the wetting of a newly formed phase at the substrate appears [77].

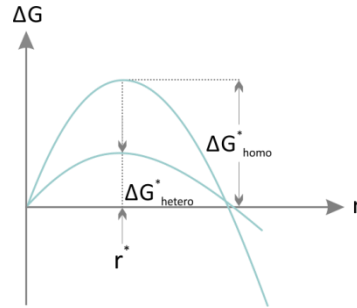


Figure 1.8: The change of critical free energy at homogeneous and heterogeneous nucleation as a function of nuclei radius [77].

Heterogeneous nucleation starts at the energetically favorable sites and a new phase forms a cap-shape nucleus on the substrate surface, followed by a subsequent growth. The growth is controlled by surface diffusion and it occurs when growth units from the surrounding supersaturated solution diffuse on-to the surface of the nucleus and get built into the crystal lattice. Incorporation of growth units into the crystal lattice is illustrated in Figure 1.9 [77]. Every crystal, even the well-polished and clean single crystal surface has imperfections such as kinks, steps and terraces. According to Kossel, growth units

attached to the steps or kinks will form two or three bonds, whereas those attached to the surface will form only one bond. Thus, if looking from the energetic point of view kinks are the most favorable sites for the incorporation of growth units, whereas terraces would be the least favorable. Incorporation of growth units onto the growing crystal depends on the surface diffusion rate. If surface diffusion is slow, growth units can incorporate on the surface at kinks and steps but it is also possible that several growth units meet on the terrace and form a cluster with several new steps and kinks. Incorporation at kink site is repeatable because one occupied kink will provide another new kink, which will be then occupied by another growth unit and so on, until the completion of the layer. However, empty sites, vacancies in the crystal lattice of the growing crystal can be formed due to imperfect stacking of growth units [75], [78].

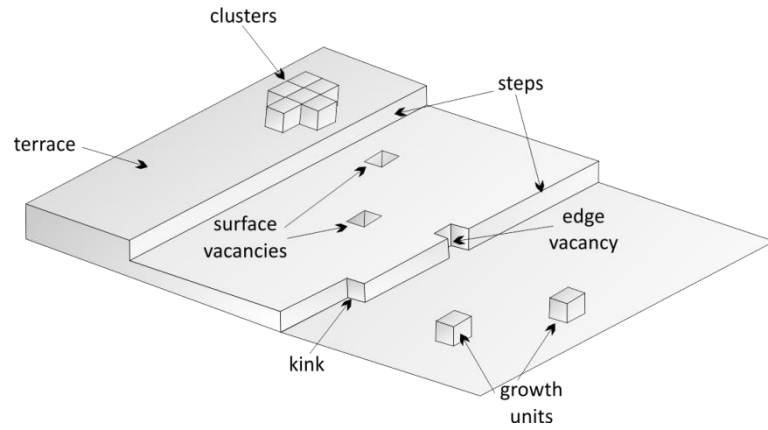


Figure 1.9: Elements (kink, step, terrace) of the surface morphology on a well-polished single crystal surface and incorporation of growth units into the crystal lattice of a growing crystal [75].

Growth modes of thin films can thus be divided into homoepitaxy and heteroepitaxy. Epitaxy alone refers to the formation or growth of single crystal (film) on top of another single crystal (substrate). The orientation of a newly grown crystal is determined by the underlying crystal. The main difference between homoepitaxy and heteroepitaxy is in the kind of underlying structure and in the type of growing. Homoepitaxy refers to the case when the growing material is the same as the substrate, whereas in heteroepitaxy the growing material differs from the substrate [77].

1.2.2 Nucleation and non-classical growth of mesocrystals

According to the classical crystal growth theory, atoms, ions, or molecules (growth units) are being considered as the basic building blocks for nucleation and subsequent growth of energetically stable crystals by the Ostwald ripening mechanism (Figure 1.6). Beyond the LaMer curve new phenomena associated with the formation of mesocrystals has been observed. Nanocrystals that form in the solution following the LaMer curve tend to self-align into mesocrystal assemblies which challenged researchers to reconsider the classical crystal growth mechanisms in nanoscale systems [81]. Thus, a new growth mechanism in which the nanoparticles are considered as the building units for the assembly of mesocrystals was identified. Self-assembly of nanoparticles by their oriented attachment (OA) was first proposed by Penn *et al.* (1998) [36] who investigated the assembly of anatase TiO_2 nanocrystals formed by the HT synthesis. Building on this initial study, Cölfen *et al.* (2005) [1] suggested this new, non-classical growth mechanism for the formation of mesocrystals (Figure 1.10). In contrast to classical crystallization,

nanocrystals that form by homogeneous nucleation self-assemble through coalescence and alignment of precipitated nanoparticles along common crystallographic planes into complex mesocrystals. In this process, primary nanocrystals, the building blocks needed to build mesocrystals, first form following the principles described in Chapter 1.2.1. With classical crystal growth they reach their equilibrium crystal shape (ECS) that further allows their assembly into mesocrystals (stage III in Figure 1.10). After the formation of primary nanocrystals and their assembly into mesocrystals the concentration of growth units (atoms, ions or molecules) decreases below $c_{\min}$ but remains higher than c_o . According to the LaMer model (Figure 1.6) nucleation is stopped, however this still allows further classical growth of the existing nanocrystals into ECS which enables their further assembly into mesocrystals. Finally, mesocrystals grow by two simultaneous processes: (i) classical crystal growth until the concentration of growth units drops below c_o (stage IV in Figure 1.10) [26] and (ii) assembly, of primary nanocrystals, until they remain present in the system.

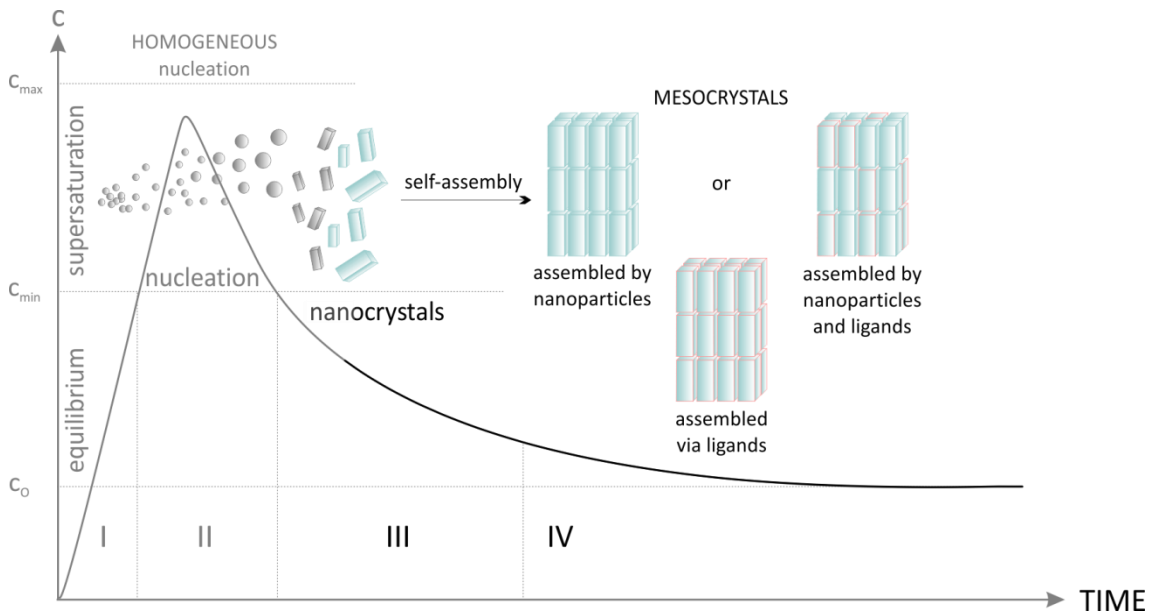


Figure 1.10: LaMer's model of nucleation and subsequent self-assembly of primary nanocrystals *via* alignment of nanoparticles, ligands or a combination of both [37].

Design of mesocrystals thus requires the control over the two main stages of mesocrystal formation: (i) nucleation of ECS nanocrystals and (ii) their assembly. While control over the crystallization process is necessary to design the size and morphology of nanocrystals by the classical crystal growth, oriented attachment (OA) provides the mechanism for their spontaneous assembly into mesocrystals. Final mesocrystals can be merged through electrostatic interactions between the nanoparticles or assisted by surface ligands (organic additives, solvent, amorphous material, *etc.*) or both (Figure 1.10). If the inner surfaces of merged nanocrystals are not stabilized, a mesocrystal can easily transform into a single crystal by fusion of nanocrystalline building blocks (Figure 1.1). This usually happens spontaneously or by the temperature increase, where the interior of this kind of crystals remains full of voids and pores filled with unreacted material such as precursors, ligands, *etc.* [82]. Depending on perfection of their assembly, mesocrystals are often misinterpreted as single crystals, especially due to their well-defined faceted appearance and single crystal scattering properties [83].

1.2.2.1 The driving forces of self-assembly

Self-assembly is a process driven by diverse interactions that generate mesocrystalline structures composed of nanocrystal building blocks. Generally it is coupled with energetic tendency of minimizing high surface energy planes, where the final mesocrystal consists of a reduced interfacial energy. Although large cumulative surface of nanocrystals may be a plausible driving force in many systems, it does not explain what makes two nanocrystals move towards each other and choose a specific orientation. Generally, the overall process includes some sort of long-distance forces that first align nanocrystals to each other assisted by thermal motion (Figure 1.11 - a), whereas short-distance forces finally lock them with the intrinsic crystal field that is specific for individual crystal structures, where they finally attach with a zipper-like mechanism into well-defined mesostructures (Figure 1.11 - b) [84].

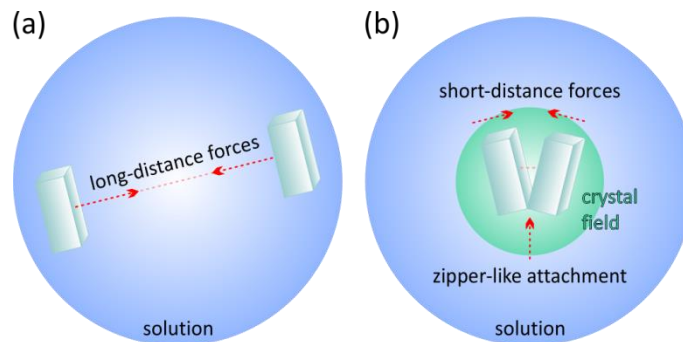


Figure 1.11: (a) Alignment of nanocrystals in solution by the long-distance forces and (b) their attachment guided by the short-distance forces and the surrounding crystal field.

Despite all the effort, understanding of the driving force of mesocrystal assembly has not evolved [85]. One of the main reasons is their complexity and the lack of experimental evidence that would lead to a theoretical consensus on its nature (Figure 1.12). Nevertheless, till now it is clear that the net driving force is usually a sum of many interactions, all depending on the properties of the assembling material (polarization, (an)isotropy, surface charge, free surface bonds, ligands, *etc.*) and properties of the solution (concentration, types, size and charge of ions and molecules, viscosity, dielectric constant, *etc.*) where OA is taking place. These interactions are highlighted in the following subchapters.

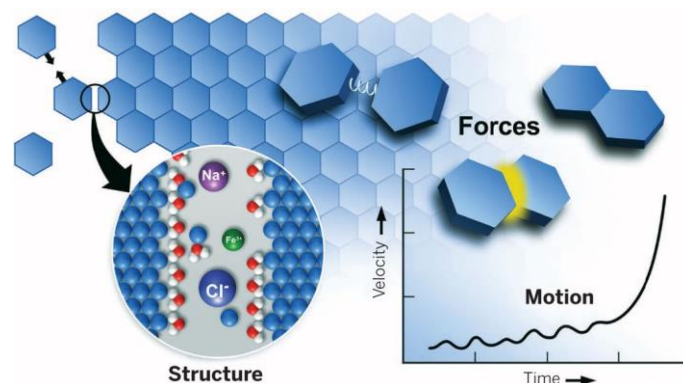


Figure 1.12: Solvent properties and the presence of ions at solid-solution and solid-solid interfaces influence the particle attachment by creating some sort of forces that drive the particle motion. By their motion, corresponding forces change, taking the particles from a

long-range to short-range interactions, which eventually lead to their oriented attachment. Adapted from De Yoreo *et al.* (2015) [85].

1.2.2.1.1 Long-range attraction forces

First, in order for a mesocrystal to form, some types of long-range interactions that act on larger distances need to align the precipitated nanocrystals relative to one another. These interactions are believed to be a result of some sort of attractive non-covalent intermolecular or ion-correlated forces that are responsible for the first step of the mesocrystal formation.

1.2.2.1.1.1 Intermolecular forces

Intermolecular forces are long-range non-covalent forces of attraction or repulsion between the interacting species (atoms, ions, molecules or fully grown particles). Regardless of their weak nature they are governing all the physical properties, *i.e.* boiling and melting point, surface tension, viscosity, *etc.* Non-covalent forces arise from the positive and the negative charges; if the charges of two approaching species have an opposite sign, the force between them will be attractive and vice versa. This purely electrostatic force is called *Coulombic attraction/repulsion*. The magnitude of this electrostatic force between the two charged species is directly proportional to the product of the magnitudes of those charges and inversely proportional to the square of the distance between the interacting species [86]:

$$F = k_e \frac{q_1 q_2}{r_s^2} \quad (1.8)$$

Equation 1.8 represents Coulomb's law, where F is the force, q_1 and q_2 are the charge magnitudes of approaching species, r_s is the distance between them and k_e the Coulomb's constant. According to this equation the decay of Coulombic force with increasing distance is gradual [86].

However, covalently bonded species do not carry a net charge, *i.e.* fully positive or fully negative like ionic ones, instead they may be partly positive (δ^+) or negative (δ^-), respectively. These partly positive or negative charges arise from the electronegativity of the elements, which is a chemical property that describes how tightly the electrons are bound to the atom. The higher it is, the more the element or a compound holds its electrons close and even attracts other electrons towards itself [87]. For example, in the HCl molecule, chlorine atom tends to draw the hydrogen electron toward itself, forming uneven electron density distribution. Therefore if two interacting atoms have different electronegativities, polarized species with a polarized bond, *i.e.* uneven electron density distribution will be formed between them (Figure 1.13). The magnitude of bond polarization is determined by the permanent dipole moment, which is oriented towards a more electronegative atom of the species (denoted by the arrow in Figure 1.13) [86].

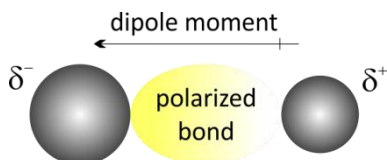


Figure 1.13: Formation of a species with uneven electron density distribution, which is distorted towards the more electronegative atom, giving rise to polarity.

From different electronegativities, *dipole - dipole* interactions of the so-called Keesom forces can arise. These are very strong anisotropic interactions that are typical for asymmetric species. They reduce the randomness of orientation and originate from the polarity of nanocrystal lattices or charged nanocrystal surface facets. If a dipole of one species is oriented in one direction, there is a high probability that attractive force will be created with a species at the site where the dipole is pointing in the same direction (Figure 1.14) [86], [88].

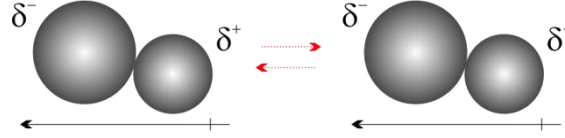


Figure 1.14: Formation of strong Keesom forces of attraction between two polarized species.

Furthermore, strong anisotropic interactions are also *dipole - induced dipole* interactions, *i.e.* Debye forces, where permanent dipole in one particle induces a dipole of opposite orientation (attractive manner) in another non-polar body [88].

Another type of intermolecular interactions are the charge-fluctuation van der Waals (vdW) forces [86] that occur due to continuous collision of negative and positive charges of the particles. Collisions arise from different strengths of electromagnetic fields and thermal agitation which creates moving charges that act on, and react to other charges and their fields, forming anisotropic polarizability [88]. These distance-dependent interactions are effective from 0.2 nm to 10 nm distances [86] and become increasingly important as the dimension of the particles decreases. They are not a result of any chemical bond and therefore quickly vanish at large distances. However, in solution, particles are always in movement by the Brownian motion, which ensures that they are colliding with each other all the time [77]. They are the sum of attractive or repulsive forces between nanocrystals with no permanent dipole, typical for symmetrical bodies. They are formed due to *induced dipole - induced dipole* interactions, *i.e.* London dispersion forces [88]. These weak isotropic forces between two instantaneously induced dipoles happen by a temporary displacement of electrons away from the electrons of a neighboring body, leading to a partially negative dipole on one body and partially positive dipole on another body at some point in time, forming an attraction [81]. It is a result of the fluctuating polarization of the nearby particles and although it contributes less to the directional arrangement of nanocrystals during self-assembly, this dispersion force is often believed to be the key that brings nanocrystals together for assembly of nanoparticles into mesocrystals [81], [86].

1.2.2.1.1.2 Ion correlated forces

When a solid is immersed in a solution, charging of a surface may be developed in three possible ways: (i) dissociation or ionization of surface groups, (ii) physical adsorption, substitution or binding of ions from the solution onto uncharged surfaces and (iii) hopping of electrons from one surface to another in a way that electrostatic attraction is established. Regardless of the charging mechanism, the final surface charge determined by the charge determining ions or co-ions (in water-based system these are OH^- and H^+ ions) is balanced by an equal amount of oppositely charged region of counter ions (all the rest of the ions, *e.g.* Cl^-). The charge densities of a surface may change from positive to negative and vice versa, depending on the variation in concentration of charge determining ions. The concentration of charge determining ions that corresponds to a

non- or zero-charged surface is determined as a point of zero charge (p.z.c.), *i.e.* isoelectric point. The surface charge density or surface potential, E that is a function of solution pH and temperature (T), can be written as [77], [86]:

$$E = \frac{2.303R_gT[(p.z.c.)-pH]}{F_c} \quad (1.9)$$

where R_g is the gas and F_c the Faraday's constant. If $pH > p.z.c.$ the surface is negatively charged, since it is covered by the OH^- ions, whereas for $pH < p.z.c.$ the surface is positively charged and dominated by the H^+ ions [77].

In the solution, charge determining and counter ions with the opposite charge to that of the determining ions are always present. Although charge neutrality and homogeneity is maintained in the solution system, the distribution of counter and charge determining ions in the proximity of the surfaces can be inhomogeneous. The concentration of charge determining ions is the lowest next to the surface and increases as the distance from the surface increases, whereas the concentration of counter ions changes in the opposite manner [77]. From this inhomogeneity the so-called double-layer structure arises, which refers to the two parallel layers of charge surrounding the surface (Figure 1.15). The first, so-called Stern layer consists of ions adsorbed onto the oppositely charged surface due to chemical interactions. Here, the electric potential drops linearly through the tightly bound layer of counter ions. The second Gouy (diffuse) layer is separated from the first one by the Helmholtz plane and consists of loosely attached ions *via* the Coulomb force (Eq. 1.8) and is electrically screening the first layer. Here, the electric potential does not reduce linearly and the counter ions diffuse freely under the influence of electric attraction and thermal motion.

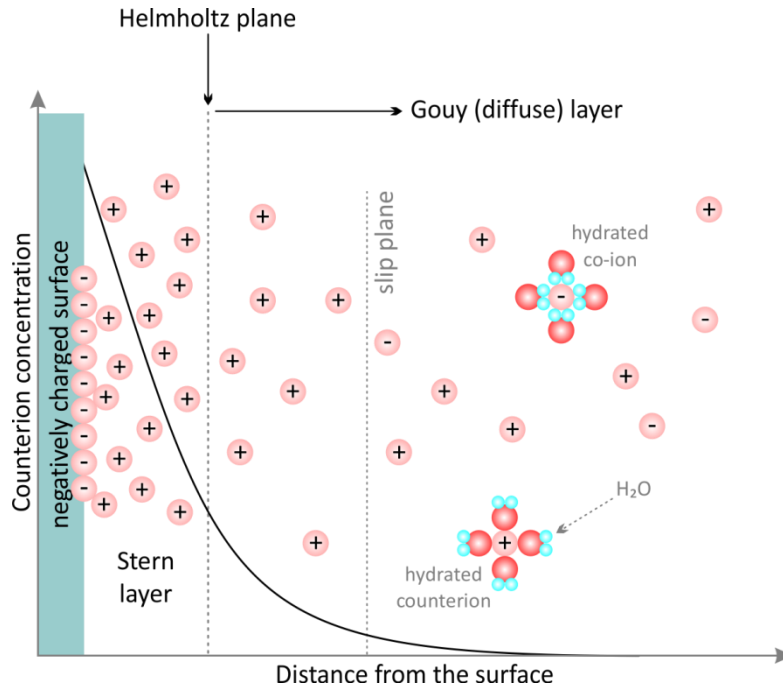


Figure 1.15: Illustration of a double-layer structure near the solid surface with both Stern and Gouy layers indicated. Co-ions, *i.e.* charge determining ions and counterions can become blocked/hydrated by the surrounding molecules, *e.g.* water molecules. In practice, double layer's thickness is about 10 nm or larger [77], [86].

If two approaching surfaces are far apart or the distance between them is larger than the combined thickness of two electric double layers of the surfaces, there would be no overlap of the diffusion double layers, consequently there will be no interactions between the two surfaces. However, when they get closer, repulsion force is developed and is increasing as the distance decreases and reaches its maximum when they are in proximity that equals the distance between the repulsive barrier and the surface. By changing chemical conditions (pH, introduction of outer anions or cations, *etc.*) of the solution and with ion condensation next to the solid surfaces, double-layer repulsion is reduced and surface potential may approach the isoelectric point [36], [89]. Moreover, mobile ions that surround the solid surfaces may produce a highly polarizable layer whose fluctuations in density give rise to an attractive *ion-correlated* force with another double-layer of the approaching surface. With this electrostatic barriers are reduced, which promotes fast and irreversible aggregation of the interacting surfaces [77]. This attraction comes into play under distances < 4 nm and it increases with the valence state of the counter ions and surface charge density [86].

1.2.2.1.2 Short-range assembly forces

Assembly forces are the same type of non-covalent forces of attraction as presented previously, but on a smaller scale. They prevail in the final step of mesocrystal formation and assure that nanocrystals attach. They are highlighted below.

1.2.2.1.2.1 Solvation forces

The term solvation (or hydration if the solvent is water) refers to the interaction of different species (atoms, molecules, complexes, surfaces, particles) with a solvent that surrounds them. The nature and strength of these interactions directly influence the solvent's properties, including viscosity and density, as well as the properties, such as reactivity and solubility. Generally, this process describes the organization of the solvent around one species and gives rise to specific *solvation forces* [86]. Solvation forces are strong, short-range oscillatory forces present between two approaching species in a medium (Figure 1.16). Usually they appear when the species are separated for less than a nanometer. These forces are a consequence of a difference between the solvent ordering or/and density in the gap between the species and in the liquid medium that surrounds them. If there is no difference, there is no solvation force. They exceed vdW forces at separations below 5-10 molecular diameters [90].

Solvation forces include several effects different from that of isolated species in vacuum or in gas. They are many-body interactions that include (i) specie-specie, (ii) solvent-solvent and (iii) specie-solvent interactions. Each of these interactions exhibits oscillatory behaviors that are correlated, *i.e.* specie-solvent interactions will affect the ordering of solvent molecules around it, which in turn affects the (i) and (ii) types of interactions. The strength of these interactions not only depends on the properties of the solvent (purity, mixtures, polarity) and its molecular geometry (inertness, sphericity, rigidity, flexibility, symmetry, linearity), but also on the physical and chemical properties of interacting species (surface roughness, curvature, overall geometry, homogeneity, crystallinity, *etc.*) that mainly affect the structure and density of the "trapped" liquid between the two interacting species.

In the case of two interacting surfaces (Figure 1.16), solvation force arises from the variation in the reorganization of the liquid molecules with separation D , which is dictated by the surface geometry. For simple spherical molecules between two hard and smooth surfaces at the atomic level, the solvation force is usually a decaying oscillatory (not sinusoidal) function of distance, varying between attraction and repulsion, with a

periodicity equal to the mean diameter of the liquid molecules [90]. The maximum of attraction occurs at the separations where the molecules can pack more densely, whereas the maximum of repulsion occurs where each packed layer opposes to squeeze out of the gap, which in turn must occur in order for surfaces to attach [90]. If two surfaces are pressed together quickly, crystallization may not happen and the molecules have no time to escape the gap, they stay locked in a nonequilibrium configuration.

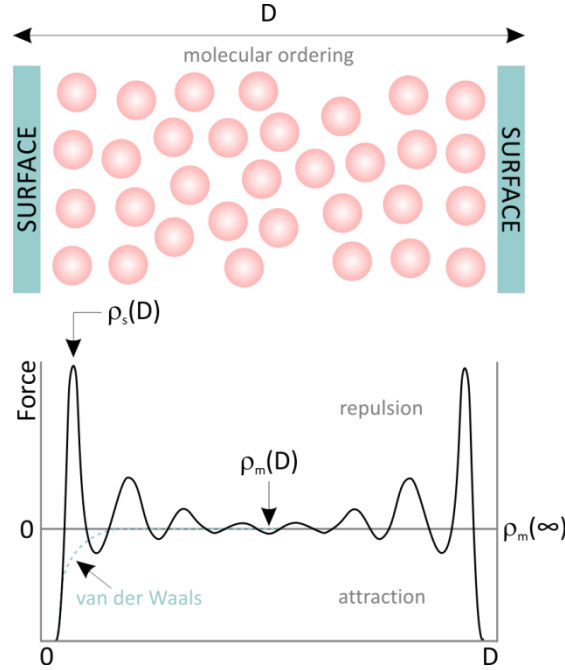


Figure 1.16: Liquid density profile between two ideally flat surfaces separated by a distance D , where layering of the liquid is reflected in an oscillatory density profile varying between repulsion and attraction and can extend several molecular diameters into the liquid. Dotted line represents predicted vdW attraction. $\rho_m(\infty)$ is the bulk liquid density, whereas $\rho_s(D)$ and $\rho_m(D)$ the contact and midplane densities that are a function of D . Higher oscillations (ρ_s value) mean denser molecular packing at the surfaces, *i.e.* strong attractive interactions between the surface and the liquid molecules [86], [90].

However, the example in Figure 1.16 is ideal and not truly realistic since no surface is smooth and flat at the atomic level, as well as no molecule is truly spherical. One can therefore expect more complex molecular ordering when “real” surfaces and liquids are involved. For molecules with asymmetric shapes and in the case of rough, not well crystalline surfaces, the resulting solvation force can be very complex arising from different shapes and sizes of the interacting surfaces and liquid molecules. In this case the solvation force can be monotonic, where the oscillations become less frequent and are smoothed out [86], [90]. Soft materials, such as polymers for example, usually do not exhibit any oscillations, just a single energy minimum, while rough surfaces show the interactions that are a high reminiscence of smoothly varying vdW-like attractive force at all separations (Figure 1.16) [90]. Overall, for either asymmetric or spherical molecules, for rough or smooth surfaces, the structure of liquid ordering is very sensitive to the slightest changes: a change of only 10 pm in the atomic or molecular geometry and surface roughness is able to produce dramatic changes in the overall strength of the solvation force [90].

1.2.2.1.2.2 Hydrogen bonding

Hydrogen bonding is a short-range intermolecular force that is believed to be the last acting force before the nanocrystals finally attach (Figure 1.17) [86]. This force appears at very short distances and arises when hydrogen that is covalently bonded to an electronegative atom, *e.g.* water molecule, is attracted to a species with at least one lone pair of electrons (Figure 1.17). If the hydrogen is bound to highly electronegative atoms such as fluorine, oxygen or nitrogen, it becomes so partial positive that the others become very partial negative, which produces even a higher amount of attraction compared to long-range dipole-dipole interactions or vdW interactions. The strength of hydrogen bonds lies in between 10 – 40 kJ/mol, whereas the strength of a typical vdW bond is only 1 kJ/mol [86].

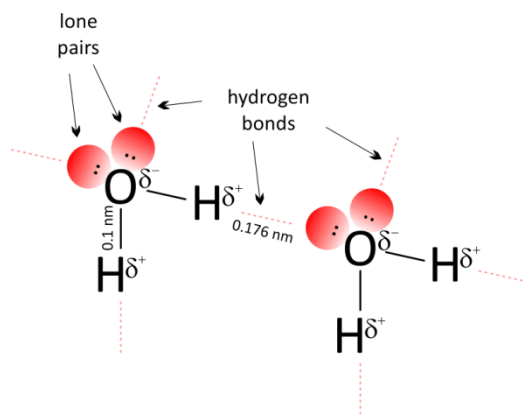


Figure 1.17: Formation of strong hydrogen bonding between two water molecules, where both of them have the capability of four hydrogen bonds formation with surrounding species [91].

On the contrary with other forces, hydrogen bond can also exist as an intramolecular force, *i.e.* force (0.1 – 0.2 nm of separation) that keeps a molecule together by a chemical bond [86], which occurs within one single molecule [86]. For this to happen, it has to have at least two functional groups that can form hydrogen bonds with each other. Intramolecular hydrogen bonding can occur for example in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups [91]. Intramolecular covalent O–H bond measures about 0.1 nm, whereas intermolecular non-covalent O...H bond is not much larger and measures only 0.176 nm (Figure 1.15) [86].

1.2.2.2 Determined driving forces in diverse nanocrystal systems

In the literature, forces presented in the previous Chapter are believed to play a major role in directing the self-assembly process. In this Chapter, these forces, reported for specific nanocrystal systems are discussed.

Zhang and Banfield (2014) [92] reported that the Coulombic interactions are being the primary physical force that drives the self-assembly process in vacuum, as well as in aqueous solutions but only when the particles are already in close proximity. If the particles are far apart, Coulombic interactions become screened out by the solution ions, and vdW interactions prevail. Anticipating that Coulombic interactions direct the growth of nanorods by OA, He (2014) [93] showed that moderate synthesis temperatures, dilute nanoparticle systems, and proper charge densities are thermodynamically favorable for the growth of long nanorods by OA. On the contrary, many authors suggested that polarized particles and induced charges control particle attachment, and hence dipolar

interactions are the key driving force responsible for OA [1], [7], [8], [41], [54], [83], [94]. However, there is a vast number of centrosymmetric structures, *e.g.* rutile- and anatase-type TiO_2 , that have no permanent dipoles and yet they are assembled into mesocrystal structures. Studying spherical BaTiO_3 , Yasui *et al.* (2015) [95] showed that the role of dipole - dipole interactions becomes increasingly important as the crystal sizes increase (~ 20 nm), since the dipoles are being scaled-up with particle's volume [81]. Accordingly, by means of electron holography, Simon *et al.* (2006) [94] showed that the phase-map image of fluorapatite crystal (> 1 μm) coincides surprisingly well with its growth sectors, and suggested that intrinsic electric dipole fields play a key role in mesocrystal assembly. On the contrary, when particles are small (< 5 nm), dipole-dipole interactions are not directing self-assembly anymore [95]. Instead, vdW torques, which appear when the particles have an anisotropic shape or are birefringent [96], associated with Brownian motion, start to direct the assembly [95]. In the recent publication by Zhang *et al.* (2017) [97], vdW dispersion forces were recognized as the principal source of interparticle attraction by the use of ETEM-AFM techniques. This study for the first time demonstrates that at short separations for dielectrically anisotropic nanocrystals, vdW torques that rotate nanoparticles into alignment can arise, regardless of the intervening water layers.

Using molecular-dynamics simulations, Fichthorn *et al.* (2009, 2015) [84], [98] made a genuine attempt to bridge atomistic and continuum principles involved in organized assembly of nanocrystals. In her case study Fichthorn used anatase TiO_2 nanocrystals to investigate mechanisms of OA in vacuum and aqueous medium. First, by eliminating the ligand effects of the medium, she demonstrated that regardless of their symmetry, rather than dipole-dipole interactions, the crystals are aligned in accordance to their intrinsic electric fields produced between under-coordinated atoms on the crystal facets. It was found that the particles adopt their final orientation when the shortest distance for the larger nanoparticles (dimension of 6 nm) between two atoms is $\sim 0.7 - 0.8$ nm, whereas by reducing the nanocrystals' dimensions (dimension of 3 nm), the shortest distance decreased to $\sim 0.5 - 0.6$ nm. The largest forces occurred for the atoms that direct the attachment, which was most commonly observed between positive $\{001\}$ surfaces (presence of four- and five- coordinated titanium atoms) and the edges between two negative $\{101\}$ planes (high density of two-coordinated oxygen atoms) seen in Figure 1.18 [98].

In aqueous medium the interactions become more complex. Ligands and complexes adsorbed on the surface of nanoparticles prevent their immediate aggregation, allowing the nanoparticles to explore many possible configurations within interacting electric fields before they are attached. During this process many transient bonds are formed and broken, if configuration is energetically unstable. Here, the process is slower than in vacuum. After crystals make the initial contact, they tend to stay in a loosely associated state making many transient contacts until they come into a close contact (0.3 nm) with parallel facets. When the crystals are finally met in low energy configuration, they are further attracted by interacting crystal fields and fixed in position by hydrogen bonds. In this state, they tend to explore numerous orientations by sliding their surfaces relative to one another, until they find the lowest energy position and fall into alignment by OA, while dehydration reactions take care of removal of dissociative and molecularly adsorbed water molecules. Finally, more stable oxygen bonds are formed in a zipper-like mechanism that closes down the interparticle gap and fixes the crystals in particular orientation [84]. It is important to note that here, OA most frequently involves the planes that have the highest propensity to dissociate water molecules, *i.e.* $\{112\}$ and $\{001\}$ surfaces of anatase-type TiO_2 [99]. This is supported by the fact that final hydrogen bonding requires adsorbed hydroxyls and not adsorbed molecular water. Along

with this study, similar continuous rotation of iron oxyhydroxide and Pt_3Fe nanoparticles while still separated by a nanometer of solution were observed by Li *et al.* (2012) [100] and Liao *et al.* (2012) [101] by the *in-situ* liquid HRTEM.

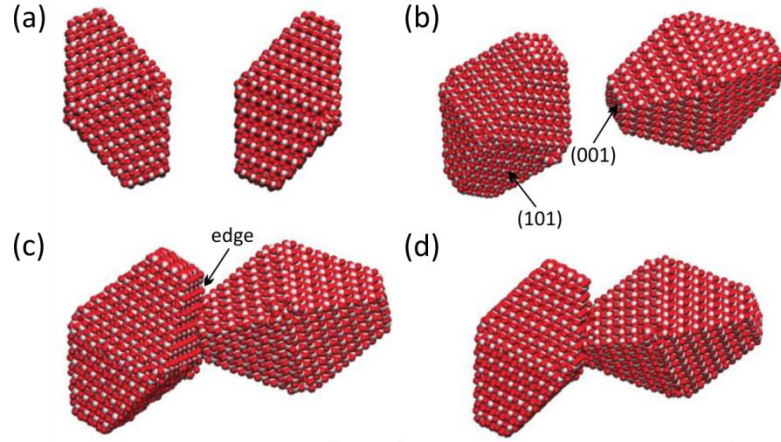


Figure 1.18: Snapshots of symmetric nanocrystal attachment. (a), (b) Assembly starts by the long-distance alignment between the two approaching particles (a – beginning and b – after 100 ps) and continues by the short-distance attachment along (001) plane of one nanocrystal and the edges between two {101} planes of another crystal, following the zipper-like mechanism (c – after 160 ps and d – after 1.0 ns). Titanium atoms are shown in white, whereas oxygen atoms in red [98].

Numerous other experimental and theoretical studies stressed out that OA most commonly takes place under the conditions of ligand-assisted crystallization, when the particles are electrostatically charged [8], [19], [102]–[106]. Here, charged capping ligands play an important role in preventing uncontrolled agglomeration [107] of particles by attractive vdW forces, while thermal agitation assists their rearrangement into low-energy configurations [1], [83]. Javon *et al.* (2015) [106] studied the interactions between Al-doped ZnO nanocrystals in solution and concluded that very strong ligand-ligand forces can overcome long-range repulsive electrostatic forces between the ZnO's intrinsic dipoles. Moreover, Zhu *et al.* (2018) [23] confirmed that binding energy of ligands on the surfaces of gold nanoparticles is the intrinsic reason for the preferential alignment along specific planes, *i.e.* the lower the ligand's binding energy on one plane, the higher the affinity for the assembly along this facet. Specifically for this case, the lower the surface energy of one plane; the lower also the binding energy of ligands on this plane, making the assembly process between the particles more favorable due to the easier desorption of ligands from the surfaces. If the binding energy is strong, this process is hindered. Moreover, rotation of particles is random at a separation distance greater than twice the layer thickness of adsorbed ligands, whereas when the particles get closer (distance of 1.3 nm), the ligands overlap and guide their rotation, until a sudden contact accompanied by the removal of the ligands from the interparticle gap occurs at the separation of 0.7 nm. According to this study, surface ligands not only serve as good stabilizers to prevent uncontrolled agglomeration of nanoparticles, but may facilitate OA along specific planes. The origin of particle's electric field and resulting surface polarization when exposed to ionic medium is therefore intrinsic and stems from the crystal structure. Furthermore, Li *et al.* (2017) [108] recently reported on attraction forces between {001} rutile planes as a function of their mutual lattice orientations and surface hydration, using AFM techniques. This study revealed that regardless the surface hydration, attractive force is

orientation-dependent, being much stronger for surfaces with water layers than without at short distances (0.35 - 0.4 nm). It was concluded that orientation-dependent attractive force is mediated by the water layers and with it connected formation of strong hydrogen bonds.

In addition to the discussed driving forces of self-assembly, some researchers proposed solvation forces [109] and ion correlated forces [110], as the driving forces for nanoparticle's alignment. As discussed in Chapter 1.2.2.1.2.1, short-range solvation forces usually vary between attractive and repulsive as the particles rotate, however they can still be strong enough to align the particles with preferred orientation relative to one another, until energy minimum is achieved where they finally diminish and the attachment occurs [109]. On the contrary, attractive long-range ion correlated forces accompanied by the vdW interactions arise only at a specific pH, where they overcome the electrostatic repulsions and initiate OA. For example, dielectrically isotropic anatase-type TiO_2 nanoparticles assemble by the OA only at pH 2.5 - 3.5, whereas all the other values lead to random aggregation [110]. As opposed to anatase, rutile-type TiO_2 is dielectrically anisotropic, *i.e.* orientation specific vdW interactions are expected to play a more important role in particle attachment as for anatase-type TiO_2 [110].

To date, the intense research revealed that growth by OA in solutions is a sum of different driving forces that mainly depend on the medium and intrinsic crystal structure. To unravel the mystery behind the driving forces of self-assembly, further theoretical and experimental studies are needed.

1.3 Mesocrystal Branching

Sophisticated architectures, consisting of highly oriented smaller crystalline subunits can nowadays be prepared in the form of 1D, 2D or 3D mesocrystals [1] with rod-, chain-, sphere-, cube- or 3D branched-like morphology [8], [21], [34], [50], [58], [111]–[116]. Among them, tunable 3D branched morphology exhibits unique, highly crystalline geometrical features with the resulting properties, superior to their nanocrystalline, polycrystalline or single crystal counterparts [70], [71]. Compared with one- or two-dimensional particles, 3D branched mesocrystals show many advantages, including hierarchic nanoparticle alignment with increased surface area, capacity and porosity, adaptable structural hierarchy and surface properties that enable short electron and mass transport pathways [112]. These properties hold a premise to finally fulfill a wide variety of application requirements and to dramatically improve the efficiencies in numerous nano-applications [70], [112].

1.3.1 Synthesis methods

With the development of material's science and nanotechnology, it is becoming more and more realistic to produce mesocrystals with a precisely defined shape, morphological complexity, as well as desired chemical and physical properties. Controlled design of versatile materials can nowadays be achieved *via* two different synthesis paths, *i.e.* top-down or bottom-up approaches (Figure 1.19). The latter is based on the preparation of nanoparticles from atoms and/or molecules, whereas in the top-down approach, nanomaterials are formed from bulk materials [117].

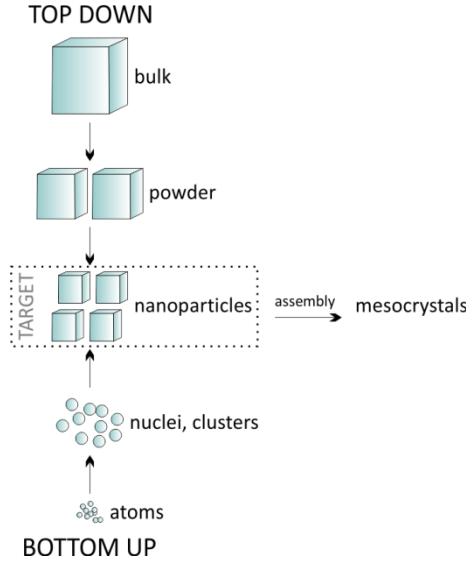


Figure 1.19: Top-down and bottom-up approach towards nanoparticles and their ordered assembly into mesocrystals.

Top-down approach is driven by physical help from the external surroundings, such as milling or attrition, mechanical grinding, annealing, laser ablation, pyrolysis, *etc.*, while on the other hand, bottom-up approaches include hydrothermal (HT) [118], solvothermal (ST) [119], [120] and molten salt [121] synthesis routes, chemical [122] and physical [123] vapor depositions (CVD and PVD), chemical solution deposition (CSD) [124], electrodeposition (ED) [125] and others [112], [120]. While top-down syntheses exhibit a few drawbacks, the most important ones being the purity and homogeneity of final powders, bottom-up approaches have already proven to be a superior choice in order to control the growth of 3D branched inorganic materials [126], such as Si [127], GaP [128], GaSb [129], SnO_2 [130], PbS [131], FeSi [132], Zn_3P_2 [133], *etc.* [134]–[136]. Their syntheses and formation mechanisms were established, however none of them offers the control over OA mechanism needed to produce branched mesocrystals. To design mesocrystalline 3D nanostructures control over the two mechanisms, *i.e.* nucleation and self-assembly of first precipitates, is required. Control over crystallization process is needed to design a crystal shape and morphology, while OA provides a mechanism for controlled assembly into mesocrystalline structures with a high degree of crystallographic registry between the individual subunits, which is not possible with any other mechanism.

Although there are many materials that can be self-assembled into a mesocrystalline structure (Table 1.1), synthesis of 3D branched mesocrystals by the OA mechanism on the other hand is much less common. To the best of our knowledge, only few materials were prepared in the form of 3D branched mesocrystals (Figure 1.20) following the OA mechanism, *e.g.* ZnO [137], Goethite [138], Au [139], Fullerene [140], $\text{Li}_2\text{FeSiO}_4$ [141], MnOOH [142], $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ [111], PbS [48] and TiO_2 [113]. Among established syntheses, solution-based processes, such as hydrothermal (HT) and solvothermal (ST) syntheses, offer better control and homogeneity of precipitated nanocrystal building blocks and their subsequent assembly process *via* OA into mesocrystals. In order to produce hierarchically branched mesocrystals, solution-based processes, such as ST or HT synthesis, should therefore be implemented. Both of them are presented and discussed in more detail in the following subchapter.

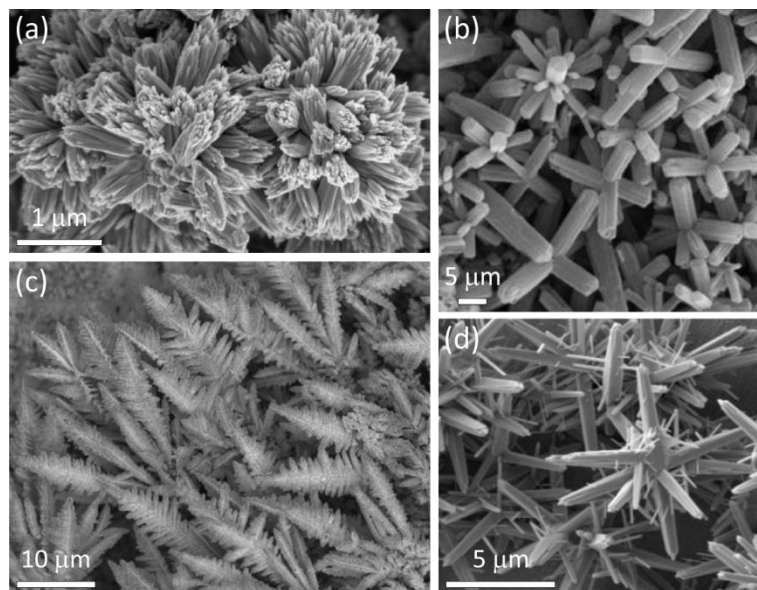


Figure 1.20: Synthesized 3D branched mesocrystalline architectures by the solution-based approaches: (a) ZnO [137], (b) Fullerene [140], (c) Au [139] and (d) rutile-type TiO_2 mesocrystals [143].

1.3.1.1 Hydrothermal (HT) or solvothermal (ST) synthesis

HT synthesis was initially employed by geologists with the aim to better understand mineralization processes. The term “hydrothermal” arises from Greek words “hydros” meaning water and “thermos” meaning heat. The first one to use this term to describe the impact of water at elevated pressures and temperatures on the changes in the earth leading to the formation of unique minerals and rocks was British geologist Sir Roderic Murchiston [144], [145]. The first work where HT synthesis was used as a technique to produce fine quartz crystals was published by Schafhaul in 1845 [145]. In the following years, HT synthesis became recognized as a leading technique to mimic natural conditions for the fabrication of numerous minerals.

HT crystallization is a solution-based method for the synthesis of individual crystals based on the solubility of a substance in water at elevated pressures and temperatures. Instead of water other organic solvents can be used. Such reaction is then termed as solvothermal (ST) synthesis. This type of synthesis is based on changing the solvents properties at elevated temperature and pressure conditions, where materials, which are originally stable and insoluble in a particular solvent, dissolve and later recrystallize. Additionally, the synthesis is used for carrying out chemical reactions such as sol-gel processes, where a solid material is produced from small molecular precursors. It involves a few formation steps that are described in more detail in Chapter 1.4.2.1. Conditions that allow the execution of these processes are typically achieved in autoclaves (Figure 1.21), either by the increase in surrounding temperature, by the addition of an external gas or by the solution filling that comes into play above 250 °C. Autoclaves are usually made of leak-proof stainless steel that keeps the solution volume in the vessel constant even at higher pressures, and lined with Teflon cups that prevent corrosion and subsequent contamination of the products. Parameters that undoubtedly influence the process kinetics, as well as the properties of the final products are pH of the medium, temperature, pressure and synthesis time [145].

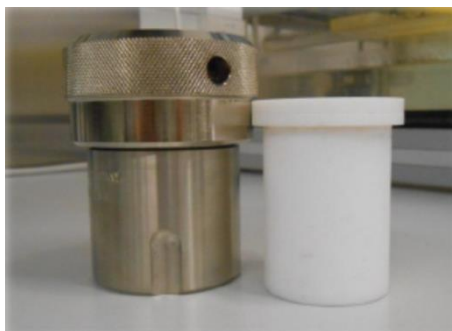


Figure 1.21: Stainless steel vessel – left, and a Teflon cup in which the crystallization reaction is taking place – right.

ST treatment offers endless possibilities by using different organic solvents in the reaction, and hence, to explore a large variety of additional parameters (polarity, molecular weight, solubility, *etc.*) [119]. On the other hand, HT approach has nowadays become widely used because of the ease of scale-up and wide choice of processing parameters. The main advantage of these syntheses are: no need for high temperatures – saves energy, products are formed directly from the reactants in the solution and are thus quite pure with a narrow particle size distribution, they can be either amorphous or highly crystalline (depending on processing conditions), pollution is minimized due to a closed reaction system, *etc.*, while the main drawbacks are the high cost of the equipment and inability to observe crystals during their growth [146].

1.3.2 The origin of crystal branching

In nature, complex intergrowths are usually produced by special crystallographic operations such as crystal twinning. This phenomenon has been observed in a variety of natural minerals, *e.g.* quartz [147], sphalerite [148], chrysoberyl [149], pyrite [150], rutile [151], [152], *etc.* and recognized as a basic tool to grow morphologically diverse structures.

In general, twinning involves a crystallographic operation that brings two crystals of the same phase into a special crystallographic relationship and unlike randomly intergrown crystals offers the capability of controlled branching. A twinned crystal is composed of two or more single crystals attached in special crystallographic orientations. They are intergrown in such a way that at least some of their lattice points coincide.

Depending on the symmetry of the mineral and the crystallographic operation imposed by the twinning, twinned crystals can be grown either as simple contact twins or form more complex twin architectures. Typical multiply twinned structures form 2D or 3D fractal-like structures, showing more generations of twinning. If they are twinned once, we observe two crystals connected with each other in a special crystallographic orientation (first generation of twinning). If further generations are formed, a twin grows on an already twinned crystal. One example of multiply twinned structures found in nature is rutile-type TiO_2 . It is observed in 2D, as well as 3D twinned intergrowths (Figure 1.22). 2D twins of rutile are formed by topotaxial replacement reactions from precursor minerals in acidic titanium-rich solutions [151], [152]. Here, due to a structurally correlated sublattice framework, rutile adopts the orientation of the parent mineral, resulting in complex crystalline networks, called sagenite by mineralogists (Figure 1.22a). Owing to the plate-like morphology of the parent mineral, sagenites are 2D, which limits their applicability. From an application point of view, branching by 3D twinning (Figure 1.22b) is preferred, however its formation mechanism still remains

poorly understood. Until today it is believed that they are formed under specific thermodynamic conditions set by HT solutions, possibly in the presence of twin-triggering dopants (Figure 1.22b) [153], [154].

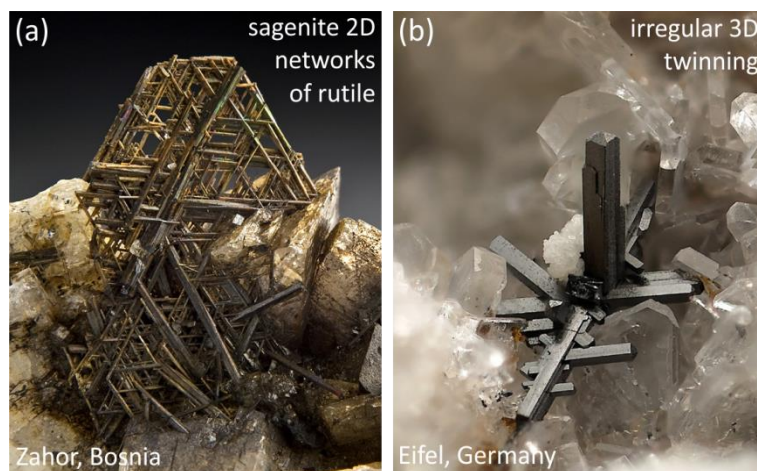


Figure 1.22: Observed in nature: (a) 2D twinned networks of rutile formed by the replacement reaction of precursor mineral and (b) 3D twinning of rutile triggered by the presence of dopants during crystal growth.

Twinning could be used as a basic structural operation for the design of synthetic twin-based branched materials. Until recently, growth twins are believed to be chemically induced [153], [154] or a result of topotaxial replacement reactions [155]. One of the mechanisms that somehow remained overlooked and not considered as a possible path for the formation of twinned architectures is OA [156]. Through interactions between the monodisperse building blocks, based on an interplay of attractive and repulsive forces among the building units (mechanism described in Chapter 1.2.2), this assembly mechanism can give rise to the formation of twins [36]. Today, OA has already proved its potential in forming twinned architectures of CeO_2 [157], SnO_2 [158], ZnO [159], [160], $\gamma\text{-MnO}_2$ [161], FePt [162], Zn_2TiO_4 [163] and TiO_2 [164]. Although the number of twinned materials obtained by the OA is increasing, none of them was yet prepared in the form of multiply branched mesocrystals, based on crystal twinning since the fundamentals of alignment and attachment mechanisms have not yet been understood.

1.4 Titanium(IV) Oxide

With their uncovering, the research of mesocrystals got a big boost, directed to the formation of branched mesomaterials with diverse morphology for a variety of applications. Although there is virtually no material that cannot be grown by self-assembly (Table 1.1), not all of them are appropriate for the design of multilevel branched architectures because not all materials have the characteristic twinning. To achieve this challenging task, the material must be chemically and thermodynamically stable and exhibit twin-like self-assembly tendency.

A material that meets these criteria is rutile-type Titanium(IV) oxide (TiO_2). TiO_2 has been present in our daily lives since its first commercial production in 1918. Today it is used as a pigment due to its whitening and opacifying properties in applications such as paper, plastics, coatings, paints, sunscreens and foods [165]. Beyond that, excellent properties of TiO_2 at the nanoscale [120], [166], facilitate its use in numerous other

applications, such as in sensing devices [167], [168], photovoltaics [120], photocatalysis [169], separation-techniques [170], [171], *etc.*

1.4.1 Properties

TiO₂ is an abundant metal oxide, which can occur in several different polymorphic forms, five of which were so far found in nature [172]. The most important ones are anatase, brookite and rutile, however TiO₂(II) [173], [174] and TiO₂(III) [175] with α -PbO₂ and baddeleyite-type structure were also reported. In addition to these, there have been reports on another six metastable high-pressure TiO₂ phases: monoclinic TiO₂(B), tetragonal TiO₂(H) with hollandite-type structure, orthorhombic TiO₂(R) with ramsdellite-type, TiO₂(OI) with pyrite-type, TiO₂(OII) with cotunnite(PbCl₂)-type structure and cubic with fluorite-type structure [166], [176].

Among all the polymorphs, anatase, brookite and rutile are the most investigated modifications of TiO₂. Their structural characteristics are shown in Table 1.2. Rutile and anatase crystallize in a tetragonal, and brookite in an orthorhombic crystal system [177]. In their structure, the basic building block consists of a titanium atom surrounded by six oxygen atoms in distorted octahedral configuration. Although anatase and rutile crystallize with the same unit cell, their octahedra which are building the crystal structure, are not the same. They have different distortions, being greater in anatase than in rutile structure. In both cases, two Ti – O bonds are slightly greater than the other four, with O – Ti – O bond angles deviating from 90° (Table 1.2). However, brookite has the most complicated structure, since there are six different Ti – O bonds and additionally, there are twelve different O – Ti – O bond angles [178].

Table 1.2: Characteristics of anatase, brookite and rutile polymorphs of TiO₂ with their crystal structures [179], symmetries [180], unit cell parameters (a,b,c) [180], Ti – O bond lengths [178] and O – Ti – O bond angles [178] presented.

Crystal form	Crystal structure	Space group	a [Å]	b [Å]	c [Å]	Ti – O length [Å]	O – Ti – O angle [°]
anatase	tetragonal	I4 ₁ /amd	3.733	3.733	9.370	1.937 (4) 1.965 (2)	77.7 & 92.6
brookite	orthorhombic	Pbca	5.436	9.166	5.135	1.87 ~ 2.04 (6)	77.0 ~ 105
rutile	tetragonal	P4 ₂ /mm	4.584	4.584	2.953	1.949 (4) 1.980 (2)	81.2 & 90.0

In all the structures, the stacking of the octahedra results in three-fold coordinated oxygen atoms. In these three polymorphs TiO₆ octahedra have different modes of arrangements. In rutile, TiO₆ octahedron is in contact with 10 other octahedra that are linked by edges and constitute chains along the c-axis. One octahedron shares two edges, four single and two double corners with adjacent octahedra (Figure 1.23a), where the edge-shared octahedra are aligned along [001] direction, forming chains that are then interlinked by sharing corner oxygen atoms to form a 3D framework. In anatase TiO₆ octahedron is in contact with 8 other octahedra, where a single octahedron shares 4 edges and 4 single corners with adjacent octahedra (Figure 1.23b). The 3D framework is generated by edge-shared octahedra that are arranged in zigzag double chains along the [100] and [010] direction [181]. Brookite has the most complicated structure where one octahedron shares both edges and corners with adjacent octahedra forming an orthorhombic structure (each octahedron shares 3 edges and a few corners with adjacent octahedra, Figure 1.23c) [182].

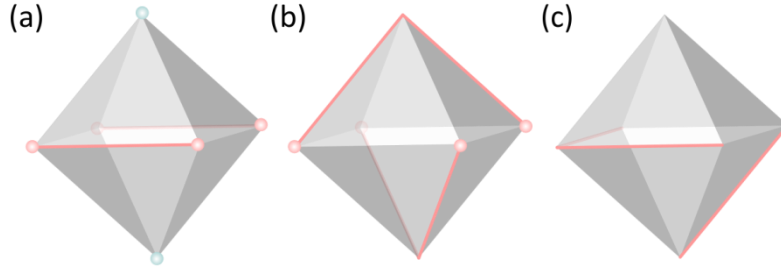


Figure 1.23: (a) Rutile octahedron shares four single corners (pink dots), two double corners (axial green dots) and two parallel edges (pink lines) with adjacent octahedra. (b) Anatase octahedron shares four single corners (pink dots) and four edges (pink lines) with adjacent octahedra. (c) Brookite octahedron shares a few corners and three edges (pink lines) with adjacent octahedra.

As a consequence of different octahedra stacking, unique properties for each polymorph arise. They are presented in Table 1.3. Rutile structure has the highest density of all polymorphs, followed by brookite and anatase. As regards the optical properties, which mostly depend on the size of nanocrystals and surface chemistry [176], both rutile and anatase have uniaxial anisotropy where one crystal axis, the optic axis, is different from the other two axes, which are equal. Brookite on the other hand has biaxial anisotropy, therefore it is not invariant under any rotation around any axis. Refractive indexes of all three major TiO_2 polymorphs are shown in Table 1.3. Rutile has the highest refractive index, whereas anatase has the lowest one. As a result of a different nature of cation-oxygen bonding in the three structures, electronic properties are different. Rutile has the lowest direct band gap of ~ 3.0 eV, *i.e.* its electrons can be excited from the valence band using only visible light spectrum (≤ 413 nm), while anatase is only active under UV-light spectrum (≤ 387 nm) with the indirect band gap of ~ 3.2 eV. Due to the difficulties of preparing brookite as a pure phase [183] its direct band gap is only an estimation, ranging from 3.1 – 3.4 eV. Among all the structures, rutile phase has the highest hardness and is the most thermodynamically stable one, whereas anatase and brookite are metastable and are known to transform to rutile upon heating [184]. In addition to temperature many researches [185]–[187] suggested that the size of a TiO_2 particle has an important role in phase transformations. Zhang and Banfield (1998) [188] thermodynamically analyzed the phase stability of nanocrystalline anatase and rutile and concluded that when the particle sizes are small enough, surface-energy effects dictate the phase of a stable particle. The border for anatase and rutile was set to 14 nm, where anatase is stable below and rutile above this boundary [188].

Table 1.3: Physical [179], [189], optical [190], electronical [172], [183] and mechanical [179] properties of anatase, brookite and rutile polymorphs of TiO_2 .

Crystal form	Density [g cm ⁻³]	Refractive index []	Band gap [eV]	Hardness [Mohs]	Melting point [°C]
anatase	3.89	2.561 2.488	3.2	5.5 – 6	Transforms into rutile
brookite	4.13	2.583 2.700	3.1 – 3.4	5.5 - 6	Transforms into rutile
rutile	4.23	2.605 – 2.616 2.890 – 2.903	3.0	6 – 6.5	~ 1850

1.4.2 Rutile

Rutile phase exhibits an exceptional combination of optical and electronic properties [166], [178], including chemical resistance and thermodynamic stability [172], [188], which makes it adaptable for a wide range of applications, such as: photovoltaic cells [143], [191], photocatalysis [192]–[194], sensing devices [167], [168] *etc.* Most importantly, it can be grown with diverse morphologies, *i.e.* rod-, sphere-, fiber-, and twin-based branched morphology (examples in Figure 1.24) that do not form in other TiO_2 polymorphs.

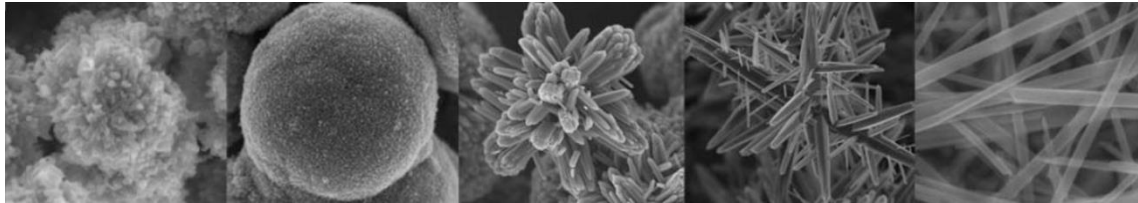


Figure 1.24: Morphological changes in rutile-type TiO_2 crystals made by the variation in HT conditions. Adapted from Zhou *et al.* (2011) [195].

Rutile's morphological versatility arises from the difference in surface energies of its crystal planes, where the ones with high surface energies exhibit the fastest growth rate and are minimized or even disappear in the final morphology. The order of growth rates in rutile-type TiO_2 is $\{110\} < \{100\} < \{101\} < \{001\} < \{111\}$, meaning that $\{001\}$ and $\{111\}$ faces usually disappear, whereas $\{110\}$, $\{100\}$ and $\{101\}$ faces are developed during growth [196]. Commonly, rutile crystals are elongated along their *c*-axis. Rutile exhibits two types of twin boundaries, with characteristic angles: (101) [152] and (301) twin [151] with 114.4° and 54.7° between the *c*-axes, respectively (Figure 1.25). According to its tetragonal symmetry this adds up to 16 possible twin interfaces, which makes rutile one of the most versatile minerals for twin-based branched growth.

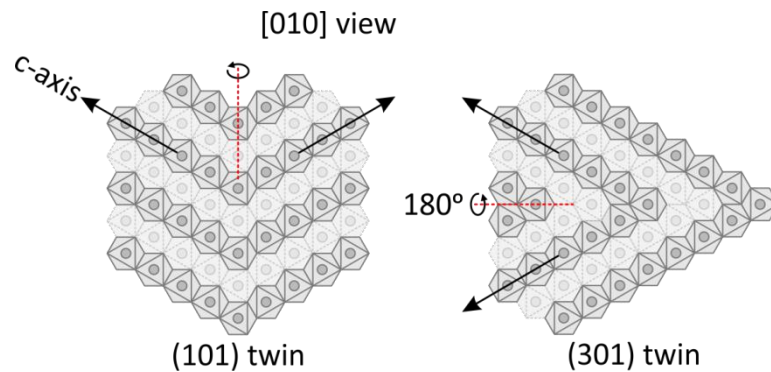


Figure 1.25: Two types of twin boundaries in a rutile structure: (101) twin – left with 114.4° between the *c*-axes, and (301) twin – right with 54.7° , respectively.

Hypothetically, by exploiting the twinning, highly branched structures could be produced, however the mechanisms of twinning are not yet explored to the extent that they could be utilized. Several synthesis paths (Table 1.4) that resulted in twin-like branched growth of rutile have been reported in the literature, however the formation mechanism is not understood. As shown in Table 1.4, branched rutile is generally obtained with the use of different titanium precursors in acidic medium, following the sol-gel process using hydrothermal synthesis. Sol-gel process is described in more detail in the following subchapter.

Table 1.4: Overview of synthesis procedures that were successful in the fabrication of twin-based branched rutile TiO_2 .

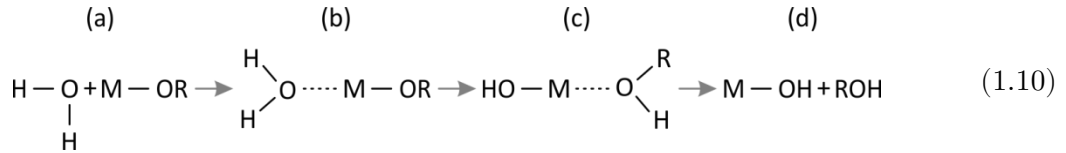
Synthesis methods	Nucleation mode	Precursor	Solvent	t [h]	T [°C]	Products
molten salt[121]	homogeneous	$\text{Ti}(\text{OH})_4$	$\text{NaCl}_{(l)}$	2	750	simple contact twins
solvothermal[211]	homogeneous	TiCl_4	toluene + oleylamine	0.5	350	simple contact twins
solvothermal[164]	homogeneous	TiCl_4	terathane 1000	72	120	simple contact twins
sonochemical[212]	homogeneous	TiCl_4	1.3 M HCl	0.8	/	simple contact twins
2-step	homogeneous	$\text{Ti}(\text{OiPr})_4$	10 M HCl	24	120	single rod-like crystals
hydrothermal[191]	heterogeneous	$\text{TiO}_2 + \text{Ti}(\text{OiPr})_4$	0.5 M HCl	4	95	multiply twinned - 1 st gen.
hydrothermal[205]	homogeneous	$\text{K}_2\text{Ti}_6\text{O}_{13}$	1M HCl	12	200	multiply twinned - 1 st gen.
hydrothermal[213]	homogeneous	Ti-glycolato complex	$\text{H}_2\text{O} + \text{glycolic acid}$	100	200	multiply twinned - 1 st gen.
hydrothermal[195]	homogeneous	$\text{Ti}(\text{OBu})_4$	7 - 8 M HCl	2	180	multiply twinned - 2 nd gen.
			5 - 6 M HCl			multiply branched
hydrothermal[208]	homogeneous	$\text{Ti}(\text{OBu})_4$	oleic acid + HCl	4	180	multiply branched
hydrothermal[115]	heterogeneous	hydrogen titanate	2 M HNO_3	48	100 - 120	multiply twinned - 1 st gen.
hydrothermal[143]	heterogeneous (glass substrate)	$\text{Ti}(\text{OiPr})_4$	6 M HCl	1 - 14	150	multiply twinned - 2 nd gen.
solvothermal[113]	heterogeneous (Si or glass substrate)	$\text{Ti}(\text{OBu})_4$	Toluene + HCl	1.5 - 12	180	multiply twinned - 2 nd gen.
acid vapor	heterogeneous	400 nm Ti film	6 - 8 M $\text{HCl}_{(g)}$	4 - 12	140	multiply twinned - 2 nd gen.
oxidation[207][222]	(Ti-substrate)	100 nm Ti film	6 - 8 M $\text{HCl}_{(g)}$	6		multiply branched

1.4.2.1 Sol-gel process

Sol-gel process includes a series of chemical reactions for producing a solid material from small molecular precursors. Usually it is induced by the increase in temperature, either in a flask or under HT conditions. The process is widely used for the fabrication of diverse simple metal oxides, such as SiO_2 and TiO_2 , as well as for the synthesis of binary oxides, such as BaTiO_3 and PbTiO_3 . Generally, there are two types of sol-gel processes, *e.g.* non-alkoxide and alkoxide process. The first approach is based on the use of inorganic acids, such as TiCl_4 as a titanium source, whereas alkoxide route includes diverse metal alkoxides as the starting material, *e.g.* $\text{Ti}(\text{OC}_4\text{H}_9)_4$ [197]. Regarding the precursor type most sol-gel processes for producing highly branched structures of rutile are based on transition metal alkoxides (Table 1.4) and less on other precursors, so the following refers to the alkoxide-based sol-gel process.

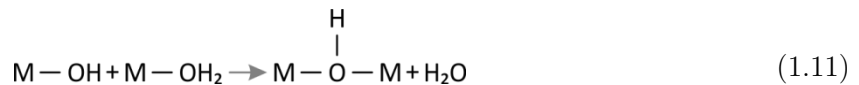
Alkoxide-based sol-gel process involves two major reactions: (i) hydrolysis of the metal alkoxide and (ii) condensation of the hydrolyzed complexes. The first reaction occurs by the addition of water molecule to the metal alkoxide $\text{M}(\text{OR})_n$, *e.g.* $\text{Ti}(\text{OC}_4\text{H}_9)_4$, where M is the metal atom (Ti), OR is the alkoxide group (OC_4H_9), R is the alkyl group (C_4H_9) and n the oxidation state of M (4^+). Hydrolysis reaction involves three steps (Eq. 1.10):

- (i) nucleophilic addition of water to the positively charged metal atom (Eq. 1.10a), leading to a transition state where the coordination number of M increases by one (Eq. 1.10b),
- (ii) proton transfer from water molecule to the negatively charged oxygen of the OR group, leading to the formation of an intermediate state (Eq. 1.10c) and
- (iii) formation of highly reactive M-OH hydroxo group by the removal of the most positively charged species (Eq. 1.10d) [197], [198].

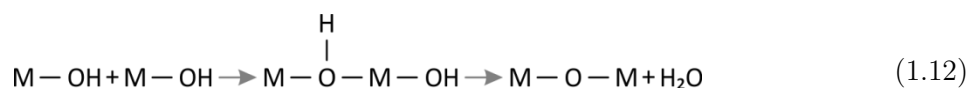


The second reaction towards an oxide's formation is the condensation process, where hydrolyzed complexes start to combine. The kind of complex that forms depends on the exact experimental conditions (degree of protonation and deprotonation), the nature of metal cation and its tendency towards the increase of the coordination number [198]. Condensation of hydrolyzed complexes takes place as soon as they are formed (if they are not stabilized) and continues until the precipitation of a solid or until the conditions allowing nucleophilic substitution are no longer present, *i.e.* partial charge of nucleophilic OH group in the complex is higher than 0 and the partial charge of the electrophilic metal cation decreases below 0.3 [198]. Nevertheless, condensation reaction can, depending on the experimental conditions, proceed following the next three possible mechanisms [197]:

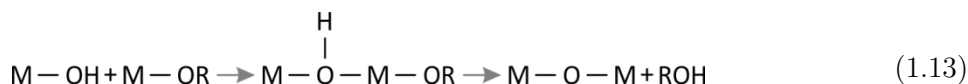
- $\therefore$ olation is the reaction between a hydroxo and aqua ligands that exist within the complexes. It leads to the formation of hydroxo-bridges through elimination of the water molecule:



- ∴ oxolation is the reaction that happens after ololation when there are no remaining aqua groups within the complexes. It is a reaction between two hydroxo ligands, leading to the formation of oxo-bridges through elimination of the water molecule:



- ∴ alcoxolation is the reaction that happens between a hydroxo ligand and alkoxide group, leading to the formation of oxo-bridges through the elimination of an alcohol molecule:



To form an oxide, oxolation or alcoxolation reactions are needed after ololation, otherwise the product remains a hydroxide [198]. Generally the elements with 2⁺ oxidation state precipitate as hydroxides and the elements with 3⁺ state as oxyhydroxides, whereas those of higher charge form an oxide with various levels of hydration [198].

Sol-gel process of metal alkoxides has been extensively studied in the case of silica, whereas for transition metals, much less data is available. Metal alkoxides that contain transition elements, such as titanium, are known to be very reactive if compared to other elements, such as silicon. The high reactivity of titanium arises from the lower electronegativity of the transition metal, as well as its tendency to increase its coordination number. Accordingly, they must be handled in a dry environment very carefully, in order to avoid unwanted reaction with water. The most important factors needed to take into account when performing sol-gel reactions are [197]:

- ∴ Hydrolysis rate decreases with the increasing size of the OR group, because the partial positive charge of the metal decreases with the length of the OR group – in order for hydrolysis reaction to take place, metal cation needs to be fully positively charged [198]. Accordingly, long and branched OR groups slow down both the hydrolysis and condensation reactions due to sterical hindrance.
- ∴ Full coordination number of a metal in monomeric alkoxides is not satisfied and it depends on the intrinsic nature of the metal cation, *i.e.* it increases with the atomic size (Ti > Si). In transition metal alkoxides the metal increases its coordination number by the acceptance of lone oxygen or nitrogen pairs from the surrounding nucleophilic ligands by using its vacant d-orbitals.
- ∴ The control over hydrolysis and condensation processes is possible by the addition of a catalyst, *i.e.* acid or base. Acid protonates negatively charged OR groups of alkoxides, making them a better leaving group, whereas base activates slow hydrolysis reactions. It is also known that the hydrolysis of silicon alkoxides can be induced by the use of NH₃ as a catalyst [197], probably by the nucleophilic activation of metal cation through the coordination of the nitrogen lone pair.
- ∴ Both reactions can additionally be controlled by the use of a very dilute system (low concentrations) and activated by the increase of the synthesis temperature.
- ∴ Metal alkoxides can be chemically modified by the use of different solvents that lead to the formation of a new modified precursor which acts differently than the original metal alkoxide.

Chapter 2

Aims and Hypothesis

The central concept of my research arises from the fact that 3D branched structures exist in nature (Figure 1.22b). One of the most well-known examples of crystal branching in nature are snow crystals that under rapid growth conditions undergo fractal-like branching [199]. The main driving force is rapid growth conditions due to supersaturation. The first response of the system is homogeneous nucleation of single hexagonal crystal seeds, followed by crystal growth. Branched growth occurs when there is an abundance of growth units available for crystal growth, leading to their preferential deposition on the fast growing crystal edges, rather than crystal faces. This happens because parts, such as edges are more close to the surrounding solution than crystal faces. For the next step of branching the same mechanism is taking place. Although this kind of growth is common in a variety of materials, *e.g.* metals [200], sulfides [201], salts [202], as well as oxides [40], it happens very fast and is consequently difficult to control. Instead of trying to direct this fast kinetically controlled growth, it seems easier to control only the parameter that actually causes branching in natural crystals (*see* Chapter 1.3.2) under defined thermodynamic conditions, *e.g.* twinning. The main hypothesis of my thesis is that the synthesis of multilevel branched materials should be possible by the sequential twinning of nanocrystals (Figure 2.1).

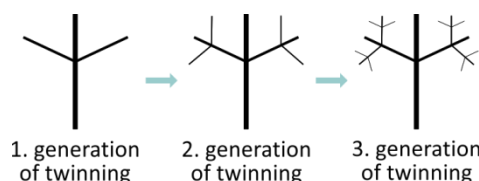


Figure 2.1: Multilevel branched structures based on sequential twinning.

2.1 Objectives

In the past couple of years many research groups dealing with crystal growth focused on the fabrication of highly branched hierarchical materials that are produced by the non-classical OA mechanism. Although OA was observed in various types of materials (*see* Table 1.1) its driving forces responsible for the formation of hierarchical structures still remain largely unexplored [85]. By understanding this complex process we would be able to produce mesocrystalline hierarchical structures that preserve the size-dependent properties of their nano-building blocks and produce materials with novel physical and chemical properties.

With this in mind, the central challenge of my doctoral thesis is to exploit twinning to produce highly branched mesostructures under defined laboratory conditions, which

could, in principle, be used in every application where a high surface area is required. Accordingly, identification and understanding of crystal nucleation and growth mechanisms are essential to control the final morphology (aspect ratio, density of branching, degree of branching, *etc.*). The results of this thesis will have an important impact on processing routes for the production of mesocrystalline rutile-type TiO_2 for diverse applications.

2.2 Outline of Results

Hypothetical 3D twin-based branched mesocrystals formation was investigated using rutile-type TiO_2 , which is a perfect candidate to exploit due to its propensity to twinning [151], [152] and self-assembly [203]. The best approach to reach these challenges is first to understand the mechanisms behind its formation, further providing the possibility to control and tailor desired morphological properties. Our objectives are divided into three main challenges:

I. Process of self-assembly: In rutile, processes of self-assembly, responsible for the formation of 3D branched mesocrystals, have not yet been clarified. Here, the complexity of their formation mechanisms was addressed by tackling the following unsolved questions:

- (i) What are the necessary conditions for producing well-defined branched mesocrystals?
- (ii) Which chemical reactions between the reagents are taking place and what is the rate determining reaction towards rutile nano-building blocks formation?
- (iii) What are the assembly modes of precipitated rutile nanocrystals into mesocrystals? The origin of branching?
- (iv) What is the role of processing parameters (acidity, concentration, *etc.*) on the formation mechanism and final mesocrystals morphology?

Identified challenges are addressed in Chapter 3 and research article:

JORDAN Vanja, JAVORNIK Uroš, PLAVEC Janez, PODGORNIK Aleš and REČNIK Aleksander. Self-assembly of multilevel branched rutile-type TiO_2 structures via oriented lateral and twin attachment. *Sci. Rep.* **6**, 24216, doi: 10.1038/srep24216 (2016)

II. Controlled branching: Until the present day, control over non-classical OA mechanism and branching was not yet investigated and established. In view of this challenge, experiments by which self-assembly was exploited for obtaining a desired spatially branched rutile were designed, which gave answers to the following questions:

- (i) How to control branching, *i.e.* what is a threshold point for the formation of ECS nanocrystals needed to generate branched mesocrystals?
- (ii) How to characterize and quantify branching?

Identified challenges are addressed in Chapter 4 and research article:

JORDAN Vanja, DASIREDDY Venkata D.B.C., LIKOZAR Blaž, PODGORNIK Aleš and REČNIK Aleksander. Material's design beyond lateral attachment: Twin-controlled spatial branching of rutile TiO_2 . *Cryst. Growth Des.* **18**, 4484-4494, doi: 10.1021/acs.cgd.8b00479 (2018)

III. Controlled processing: For any application, products should be homogeneous and the synthesis process should be reproducible. Due to the lack of understanding and non-explored ways how to control mesocrystals morphology, procedures for scale-up

production of branched 3D mesocrystals have not yet evolved. In the last part, this challenge has been addressed by answering:

- (i) How to produce reproducible and homogeneously branched rutile mesocrystals?
- (ii) Has homogeneity any influence on the specific surface area of final mesocrystals?

Identified challenges are addressed in Chapter 5 titled: Low-temperature synthesis of hierarchical rutile-type TiO_2 mesocrystals.

Chapter 3

Self-Assembly of Multilevel Branched Rutile-Type TiO_2 Structures Via Oriented Lateral and Twin Attachment

In rutile, branching has been attributed to different phenomena, including crystal splitting [204]–[206], acid-assisted surface corrosion [143], [207], heteronucleation [195], [208], anatase mediated branching [113], [208], [209] and OA [36], [210]. It was described by a few attachment laws, such as $\{301\}$ [121], [211], $\{101\}$ [113], [115], [121], [203], [208], [211], [212], $\{111\}$ [195], $\{200\}$ [203] and $\{110\}$ [203], [213] out of which the most important element is twinning. Common to these studies is that:

- ∴ branching is believed to be inversely proportional to the medium acidity and
- ∴ hydrolysis reaction is the rate determining process [195].

To clarify the processes involved in the formation of 3D branched mesocrystalline rutile-type TiO_2 , chemical reactions among reagents and the influence of the most important reaction parameters (concentration, temperature, *etc.*) on branching events were established first. Finally, with respect to the formation mechanism, the key processes that are taking place before and during HT synthesis were analyzed.

We have shown that depending on experimental conditions under HT crystallization procedures, a variety of products ranging from branched crystal clusters, nanocrystal rods and fibers, microspheres *etc.* can be synthesized. Among them, well-defined branched mesocrystals (Figure 3.1-a) show the most interesting morphology that one can achieve through higher temperature, lower precursor (titanium(IV) butoxide) concentration or lower reagent (H_2O) concentration. The key processes identified with this study, which control the non-classical growth mode of multilevel branched rutile mesocrystals are:

(i) nucleation of rutile precipitates:

Precipitates form *via* hydrolysis and condensation reactions, where the condensation reactions are the rate determining processes since hydrolysis is taking place upon immediate contact of a precursor and aqueous reaction medium. Along with precursor concentration and synthesis temperature, we showed that medium acidity is the most influencing factor already at the nucleation stage of mesocrystal formation. It not only provides the control by decelerating the rate of condensation reactions, it also determines the balance between the two associative processes, *i.e.* ololation and oxolation for producing ECS precipitates.

(ii) **irreversible assembly and growth:**

The first self-assembly mode of ECS rutile precipitates is their common assembly along low-energy $\{110\}$ crystal planes that lead to lateral mesocrystal growth.

(iii) **irreversible assembly and twinning:**

The second self-assembly mode of precipitates is their uncommon assembly along $\{101\}$ crystal planes that lead to twinning. Twinning has therefore been identified as a self-assembly process and the element that causes branching in rutile.

Our study excluded the possibility of surface energy reduction of being the driving force for OA in the case of rutile mesocrystals, since self-assembly of precipitates is taking place on already low-energy surface planes. Additionally, the presence of amorphous material between imperfectly assembled fibers by the OA is observed (Figure 3.1-b), which clearly shows the semi-ordered amorphous phase resembling that of the adjacent rutile structure. This important experimental evidence indicates the presence of force-fields that convey structural information through which OA of nanocrystals is possible.

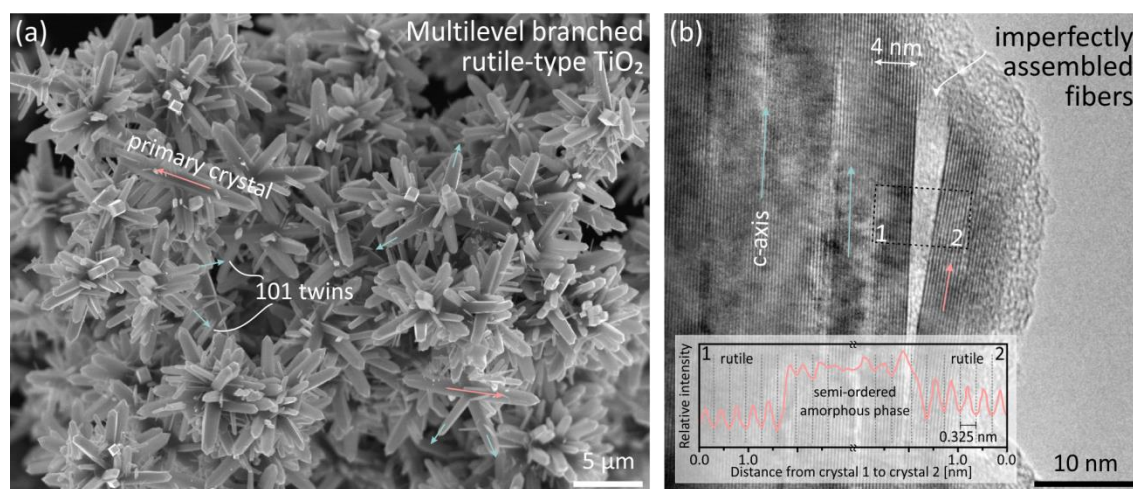


Figure 3.1: (a) FEG-SEM image of multilevel branched rutile mesocrystals HT treated at 180 °C and 3 h, using low precursor (28 mM of titanium(IV) butoxide) and low reagent concentration (4.4 M HCl) and (b) HRTEM of imperfectly aligned rutile fibers, showing the presence of semi-ordered amorphous phase.

In our study we have shown that twinned TiO_2 structures are produced by self-assembly of primary rutile precipitates on two low-energy $\{110\}$ and $\{101\}$ planes, leading to lateral attachment and twinning. The described mechanism has a potential to open the prospects of exploiting the nature of driving forces along with ECS to enforce self-sustained assembly of nanocrystals into desired crystalline architectures. More on this topic is provided in the article entitled “Self-assembly of multilevel branched rutile-type TiO_2 structures via oriented lateral and twin attachment”, written by V. Jordan, U. Javornik, J. Plavec, A. Podgornik and A. Rečnik [214]. Article is presented on the page 37, and its Supporting Information under Appendix A.

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Self-assembly of multilevel branched rutile-type TiO_2 structures via oriented lateral and twin attachment

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Recent breakthrough of novel hierarchic materials, orchestrated through oriented attachment of crystal subunits, opened questions on what is the mechanism of their self-assembly. Using rutile-type TiO_2 , synthesized by hydrothermal reaction of Ti(IV)-butoxide in highly acidic aqueous medium, we uncovered the key processes controlling this nonclassical crystallization process. Formation of complex branched mesocrystals of rutile is accomplished by oriented assembly of precipitated fibers along the two low-energy planes, *i.e.* {110} and {101}, resulting in lateral attachment and twinning. Phase analysis of amorphous material enclosed in pockets between imperfectly assembled rutile fibers clearly shows harmonic ordering resembling that of the adjacent rutile structure. To our understanding this may be the first experimental evidence indicating the presence of electromagnetic force-fields that convey critical structural information through which oriented attachment of nanocrystals is made possible.

The key issue of the emerging renewable energy technologies nowadays, is fabrication of highly efficient hierarchic/branched materials with large specific surface area, increased capacity, adaptable morphology and surface properties that enable short electron and mass transport pathways, tailored for diverse applications¹. In response to these challenges material's scientists have begun exploring non-classical crystallization routes that involve the use of organic templates and electrostatic interactions that assist self-organization of crystalline matter into desired architectures. Bottom-up design of hierarchic 3D nanostructures requires control over the nucleation and assembly of first precipitates^{2–4}. Understanding these mechanisms is essential to tailor chemical and physical properties of self-assembled materials. While the control over the crystallization process is needed to design crystal shape and morphology, oriented attachment provides mechanism for spontaneous self-assembly of branched and mesocrystal structures with a high degree of crystallographic registry between the constituent parts⁵. Self-assembly of nanoparticles is generally coupled with changing chemical conditions that drive surface potential to approach the isoelectric point^{6–8}. This, in effect, causes a reduction of electrostatic barriers and promotes fast and irreversible aggregation of the primary particles⁹. With this process the total energy of the system is decreased by the surface energy reduction associated with unsatisfied surface bonds^{4,10}, while dipole fields that exist around the primary particles are considered responsible for the unique hierarchical assembly of mesocrystals^{3,4,11,12}. Depending on the synthesis conditions the primary particles can align to each other with such a perfection that resulting mesocrystals exhibit scattering patterns resembling that of a single crystal^{4,5,13}. There is virtually no material that would be unsuitable for growing hierarchic superstructures via self-assembly, as long as the surfaces of the attaching particles are dimensionally similar¹⁰. Here, solution methods, *e.g.* hydrothermal crystallization procedures are becoming increasingly attractive because of their low growth temperature, low cost, and a simple scale-up¹⁴.

One of the most thoroughly studied materials that exhibits self-assembly and twinning, necessary for producing hierarchic fractal-like branched structures, is rutile-type TiO_2 ^{14–20}. Moreover, the rutile phase exhibits an exceptional combination of electronic and optical properties, including appropriate band-gap structure,

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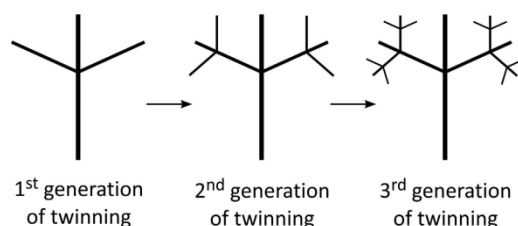


Figure 1. Multilevel branched nanostructures of rutile based on sequential {101} twinning.

thermodynamic stability and chemical resistance^{14,21–27}, which makes it adaptable for a range of applications, such as: photocatalysis^{28–31}, photovoltaics^{32–36}, sensors^{37,38}, *etc.* Branched structures of rutile are generally obtained in an acidic medium with the use of different metalorganic titanium precursors^{15–19,32–36}. Due to increased specific surface area, branched rutile nanostructures show enhanced efficiency in photo electrochemical production of hydrogen and improved solar energy conversion efficiency when compared to simple rutile nanorods^{30,32,36}.

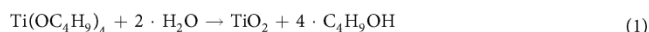
Recently, much attention is paid to the mechanisms that cause branching of rutile, being attributed to different phenomena, such as: anatase mediated branching^{15,17,19}, heteronucleation^{16,17}, acid-assisted surface corrosion^{34,39}, oriented attachment^{10,40}, coalescence twinning⁴⁰, and crystal splitting^{33,41,42}. Common to these studies is that branching of rutile appears to be inversely proportional to the acidity of the medium; where in less acidic medium the hydrolysis of the titanium (IV) precursor is believed to be more intense¹⁶, leading to forceful nucleation and formation of rutile microspheres, whereas under more extreme acidic conditions branched structures are evolved. The branching has been described by different attachment/twinning laws, including {111}¹⁶, {200}¹⁸, {110}^{18,29}, {101}^{17–20,43–45}, and {301}^{44,45}, out of which the most important element of branching is twinning. It involves simple geometric operations that bring two or more crystals of the same phase into special orientations that are not possible by random intergrowths. In rutile, twinning is a result of topotaxial reactions^{46–48}, deformation⁴⁷, or attachment^{18,19,40,49}. Following only one twinning law, *e.g.* {101}, branches in eight unique directions can be produced on the primary rutile crystal⁴³. These can be additionally twinned into complex fractal-like structures. Hypothetic multiple twinning and formation of multilevel fractal-like branched crystal clusters is illustrated in Fig. 1. While twinning is often reported in branched rutile structures, its origin is yet to be explained.

Until the present day there is no direct evidence on the origin of self-assembly and twinning of rutile. We designed experiments that helped us to identify the key processes during the formation of branched rutile structures and estimate the role of oriented attachment in crystal growth and twinning that would provide principal protocol for tailoring desirable branched morphologies (aspect ratio, density of branching, multilevel branching, *etc.*). With this in mind we studied the initial nucleation stages of crystal assembly and showed that under acidic hydrothermal (HT) conditions rutile crystals growth via oriented attachment of precipitated rutile fibers on {110} and {101} crystal planes, forming complex branched mesocrystal structures.

Results

Experimental work has been planned to identify the mechanisms that control growth and branching of rutile crystals. Foremost attention was dedicated to resolving the initial stages of crystallization. First, proton nuclear magnetic resonance (¹H-NMR) analysis of the starting solution, before HT treatment was carried out to resolve which of the two processes, hydrolysis or condensation reaction^{16,50}, is rate determining. Aggregation of precipitates nucleated after short time of HT processing was studied by transmission electron microscopy (TEM).

During HT processing the following overall reaction between Ti(IV)-butoxide (precursor) and water (reactant) takes place:



where HCl is used as a crystallization inhibitor⁵⁰. Different HT conditions, *i.e.* precursor and reactant concentrations with acidity (OH[−]/H⁺ ratio, *see* Supporting Information; Table S1 for detailed calculations), synthesis temperature and time, were studied to understand their role in final product morphology. Depending on the choice of experimental conditions, variety of products, ranging from nanocrystal fibers and rods, twinned (branched) crystal clusters, radiating crystal clusters and microspheres composed of multiple rutile crystals radiating from the common center are synthesized (*see* Supporting Information; Figure S1).

Hydrolysis. ¹H-NMR was used to verify whether the hydrolysis takes place before the HT synthesis, when Ti(IV)-butoxide is exposed to HCl. Characteristic chemical shifts of alkyl groups bound to titanium cation are nicely distinguishable (denoted by a, b, c and d in Fig. 2a). Sharp signal at around $\delta = 4.8$ ppm corresponds to D₂O reference. However, when we introduce 4.4 M HCl, Ti(IV)-butoxide fingerprint (Fig. 2a) is replaced by chemical shifts corresponding to free n-butanol (Fig. 2b), indicating that the hydrolysis step is completed already at room temperature (RT). This was confirmed by measuring ¹H-NMR spectrum of n-butanol reference (Fig. 2c). Broad chemical shift at ~ 6.1 ppm corresponds to H₂O in the form of OH[−] and H₃O⁺ groups.

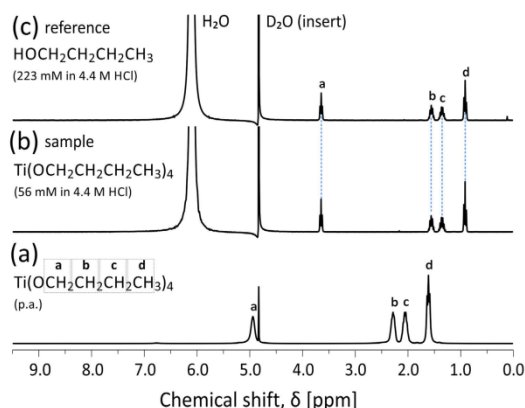


Figure 2. Spectroscopic evidence of RT hydrolysis reaction. ^1H -NMR spectra of (a) 97% Ti(IV)-butoxide (*p.a.*), (b) Ti(IV)-butoxide sample and (c) n-butanol reference (calculated to match the concentration of n-butanol that is released in the solution after complete hydrolysis).

First precipitate. In the initial stages of synthesis, that are met under low reactant concentrations, high medium acidity (low OH^-/H^+ ratio), short processing times and low target temperature, the product phases are not yet evolved. Powder XRDs of early precipitates shows two broad reflections above the amorphous background that somewhat corresponds to the anatase phase. As soon as the product has ample time to crystallize, the amorphous TiO_2 /anatase reflections disappear and sharp rutile reflections peak sharply above the background (see Supporting Information, Figure S2). Thus, final products obtained under our synthesis conditions are well crystalline, exhibiting sharp reflections that correspond to the rutile phase of TiO_2 .

To identify crystal formation mechanism the products were studied by TEM. The finest fraction of the precipitate is composed of ultrafine rutile fibers that are commonly aligned into fan-shaped bundles. Alignment of rutile fibers is observed already in the sample processed for only 30 min at the target temperature of 180°C (Fig. 3a). The length of the rutile fibers can reach up to 500 nm, while their width is just 4–7 nm. After short times of HT treatment a large part of Ti-precursor is yet unreacted (Supporting Information, Figure S2). Consequently, we find numerous isolated rutile fibers embedded in an amorphous gel-like Ti-precursor phase (inset in Fig. 3a; further details in Supporting Information, Figure S3). Due to their high aspect ratio, it is not unusual to see some fibers bent. As may be expected, electron diffraction pattern (EDP) recorded over a rutile bundle shown in Fig. 3a, confirms that the long axis of the fibers corresponds to the *c*-axis of rutile (Fig. 3b). The most interesting feature is the angular dispersion of $\{002\}_R$ reflections that is caused by systematic misalignment of fibers. Misalignment increases monotonously from the center to the rim of a bundle, in $\langle hk0 \rangle$ directions, producing fan-shaped assembly of fibers. Weak diffraction rings accompanying the strong reflections in EDP correspond to other randomly oriented nanoparticles in the area. While the majority of these rings stem from rutile there is a ring of weak reflections that best matches $\{101\}_A$ of anatase (see Fig. 3b; the ring with a slightly larger *d*-value than $\{110\}_R$ ring of rutile). These weak reflections correspond to clusters of nanosized crystallites with isometric appearance (marked with circle in Fig. 3a), indicating that anatase phase can be present during the initial stages of rutile precipitation. Energy dispersive X-ray spectroscopy (EDS) analysis over the anatase particles or rutile fibers shows no presence of chlorine (from HCl). The 30 min sample was very sensitive to the electron beam, leading to fast irradiation damage.

After 60 min of HT processing at the target temperature of 180°C , the bundles are generally larger and the rutile fibers are more firmly attached (Fig. 3c). They have poorly defined jagged terminations reflecting their fibrous texture. New features in this sample are shorter rutile rods attached at characteristic angles with respect to the direction of the *c*-axis of long fibers in the primary bundle. These attachments, reminiscent of twinning, occur at different depths in a bundle. While strong reflections in EDP (Fig. 3d) originate from the bundle, weak diffraction rings stem from the particles that are not aligned with the main bundle. Misalignment of fibers composing the bundle is reflected in an angular spread of reflections containing a component of the rutile *c*-axis, e.g. $\{101\}_R$ and $\{002\}_R$. In this sample anatase particles are no longer present.

Assembly of rutile fibers. Rutile-type TiO_2 precipitates in form of few nanometers thick fibers produce fan-shaped nanocrystal assemblies. While initially the fibers are poorly attached and their assembly appears to be weak, this is improved with time, resulting in compacting the bundles, as shown in Fig. 4. Lattice image in Fig. 4a presents the outer section of a bundle from the sample HT treated for 120 min at 180°C . In the interior, rutile fibers are assembled with such a perfection that they produce nearly ideal crystal lattice, whereas on their surface the crystals are covered by ~1 nm thick envelope of amorphous titania. Bulk rutile is intermittently disrupted with $\{110\}$ planar faults that suggest assembly of fibers along these low energy prism planes⁵¹. The distance between the faults corresponds to the average width of precipitated rutile fibers. Any mismatch is compensated by edge

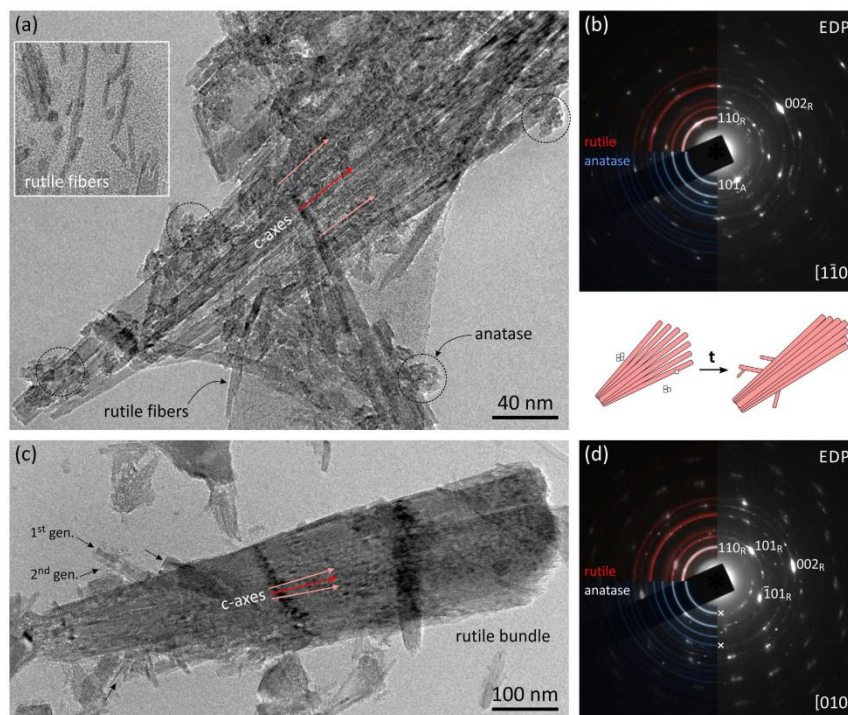


Figure 3. Self-assembly of rutile fibers. TEM of fibrous TiO₂ precipitates using 56 mM Ti(IV)-butoxide in 4.4 M HCl and a target temperature of 180 °C. **(a)** Already after 30 min the sample contains rutile fibers, roughly aligned along the crystallographic c-axis into fan-shaped assemblies. The inset (left) shows individual rutile fibers precipitated from the amorphous Ti-precursor gel. **(b)** Strong reflections in EDP stem from the assembly of rutile fibers while the rings belong to isolated rutile rods and clusters of nanosized anatase. **(c)** After 60 min, bundles of rutile fibers become more compact and younger generations of rutile with special angular relationships to the primary bundle start to appear. Anatase particles are no longer present; **(d)** in EDP, all reflections belong to rutile. Illustrations show TiO₂ products developed in the initial stages of processing.

dislocations, accompanied with accumulated lattice strain. Near terminations, the fibers can be deflected from the main crystal for several degrees (up to $\sim 7^\circ$), embedding amorphous remnants of mineralizing solutions. Facing (110) surfaces are atomically sharp, and at first glance, this might imply splitting and detachment of fibers⁴². However, at the junction between the parent rutile and the fiber, we can observe a formation of additional rutile layers that should not be present, if the crystal was split. A similar ledge growth of rutile can be also observed at outer ends of the parent rutile and the deflected fiber (indicated by circles in Fig. 4a), suggesting a late stage of crystallization rather than crystal splitting. A further evidence for mesocrystal assembly is the presence of amorphous titania enclosed in pores between the imperfectly assembled rutile fibers. A close-up of the interspace in Fig. 4b shows that amorphous material is strongly modulated by the periodicity of adjacent crystalline rutile. Averaged intensity profile across the pocket of amorphous phase shows that its periodicity does not strictly follow the (110) interplanar spacings. The observed modulation can not be a result of contrast delocalization (its effects are seen at the outer amorphous edge) nor they are wedge (same periodicity) or ledge effect that are distinctly different (outlined by circles in Fig. 4a). What we observe here appears to be ordering of mineralizing fluids, frozen in their pristine condition. This evidence suggests that during growth, crystalline matter induces some harmonic ordering that extends 1–2 nm deep into the amorphous phase.

Multilevel branching of rutile. In addition to lateral assembly of rutile fibers, multiple branching is observed under low supersaturation conditions in highly acidic medium², producing complex crystallographically interconnected 3D architectures. Figure 5 shows a typical branched cluster of rutile crystals. Regular incidences of the branches with respect to the primary crystal are indicative of well-defined crystallographic relation, such as twinning. To confirm twinning crystallographically, the crystals must be oriented into a zone axes, where the twin plane can be viewed edge-on; to view (101) twin in rutile such projections are [010], [101], [111], etc.⁴⁷ The primary crystal in Fig. 5a is oriented in [111] projection, which happens to be the most common docking of

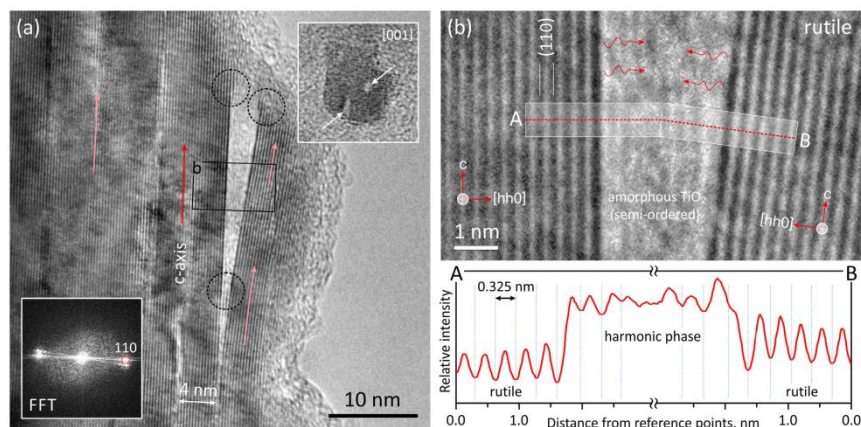


Figure 4. Oriented attachment of rutile fibers. (a) High-resolution TEM (HRTEM) image of an edge of a rutile bundle, treated 120 min at 180 °C, using 56 mM Ti(IV)-butoxide in 4.4 M HCl. In bulk rutile, many planar defects are seen along the (110) planes (Fast-Fourier Transform; FFT). The directions of the c-axes are marked by red arrows. The outer stripe of rutile is deflected from the matrix enclosing a pocket of amorphous titania. Dotted circles denote points of secondary crystallization. The inset in the upper-right corner shows a cluster of rutile fibers viewed along the c-axis. White arrows indicate the pores that remained after imperfect assembly of the fibers. (b) Close-up of amorphous titania enclosed between two rutile fibers from (a). Intensity profile over a phase-contrast image from reference points A–B shows harmonic ordering in the amorphous titania that mimics the (hh0) lattice periodicity of rutile.

branched rutiles on carbon-coated TEM grids. Because in this projection the angle between the c-axes of a branch and the primary crystal cannot be measured directly, we can use prism planes that contain the $\langle 001 \rangle$ vectors. The angle of $\sim 45^\circ$ measured from the TEM image corresponds to a complementary angle between $(110)_{R1}$ & $(110)_{R2} \equiv 134.9^\circ$, which is produced by 180° rotation around the (101) -plane normal. This operation generates (101) twin with the characteristic angle between the c-axis of 114.4° , and complementary at 65.6° ^{18–20,45,47}. EDPs recorded on the primary crystal and the branch, shown in Fig. 5c,d, confirm this crystallographic relation. On some branches we also observe a 2nd generation of branching (detail shown in Fig. 5b) that is clearly following the same crystallographic rules, as demonstrated by corresponding EDPs in Fig. 5c–f. All rutile crystals displayed in Fig. 5b ($R_1|R_2$, $R_2|R_3$ and $R_2|R_4$) are related by $\{101\}$ twin relations. Small angular discrepancies are due to imperfect fiber attachment. Nanocrystal attachments that were here identified as twinning, form in a similar process as lateral attachment, already in the initial stages of fiber assembly.

In rutile we identified two types of oriented attachment: (i) lateral assembly of rutile fibers on $\{110\}$ planes, and (ii) twin assembly of rutile fibers on $\{101\}$ planes, both related to crystallographic planes of the lowest surface energy⁵¹. Compared to lateral assembly, twin incidences are subordinated by several orders of magnitude. Through fine tuning the HT conditions, *i.e.* precursor and reactant concentrations, acidity, synthesis temperature and time, it is possible to control the equilibrium shape of precipitated crystals and their assembly rate (see Supporting Information; Figure S1). Figure 6 shows the product morphology as a function of precursor concentration, where fan-shaped crystals are formed under high supersaturation conditions, whereas well defined branched rutile structures are produced under low supersaturation conditions. By exploiting two self-assembly modes together with variation of supersaturation tailoring of multilevel branched structures of rutile, such as illustrated in Fig. 1, should be possible.

Discussion

Based on our results, a possible mechanism for the formation of branched rutile structures can be discussed. In this section we analyze the key processes that are taking place during the formation of rutile from Ti(IV)-butoxide in acidic conditions: (i) nucleation of rutile fibers via hydrolysis and condensation, (ii) self-assembly of rutile mesocrystals via fiber attachment and growth, and (iii) twinning and formation of multilevel branched structures.

Nucleation of rutile fibers. In order for any TiO_2 -based compound to be produced, the formation of TiO_6 octahedra, the basic building blocks of these structures, is necessary. The origin of their formation lies in the electronic structure of titanium. In our precursor, Ti(IV)-butoxide, $4s^2$ and $3d^2$ orbitals of titanium undergo an octahedral d^2sp^3 hybridization⁵². In this configuration, all four valence electrons located in equatorial hybrid orbitals are shared by highly electronegative OR^- ligands ($R = C_4H_9$)⁵³, while the two axial orbitals remain empty. In the presence of water, tetravalent cations hydrolyze spontaneously⁵⁴. With ^1H -NMR analysis we confirmed that even under highly acidic conditions hydrolysis of the precursor is not slowed down^{16,55}, but is completed already at the room temperature. During hydrolysis, OR^- ligands in Ti(IV)-butoxide are substituted by strongly nucleophilic

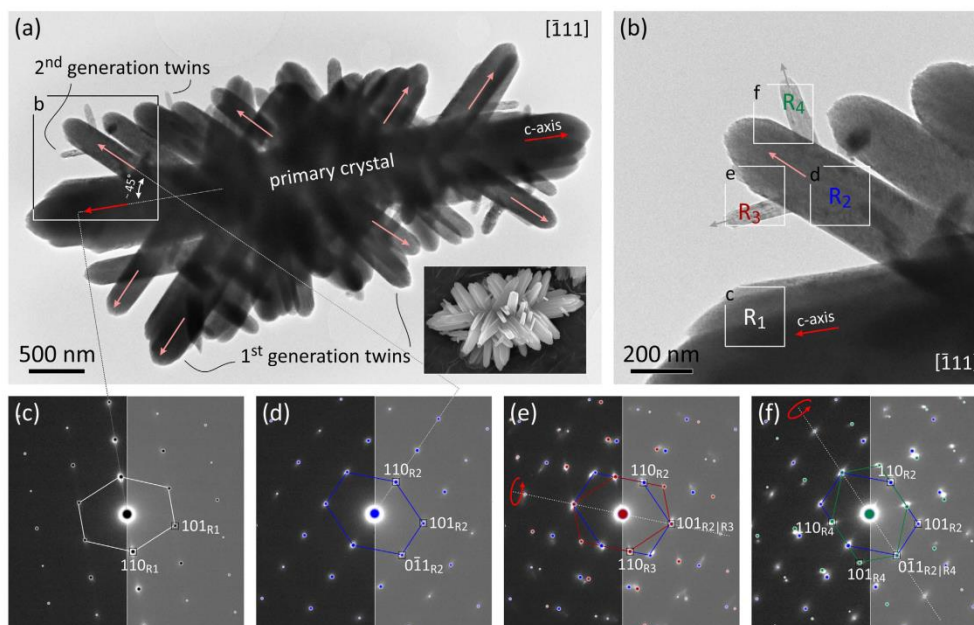


Figure 5. TEM study of twinning in multilevel branched rutile cluster. (a) Branched rutile cluster in $[\bar{1}11]$ projection with discernable crystallographic incidences. The inset shows an SEM image of branched rutile cluster. Typical angle between the primary crystal and the branches, measured between (110) planes is $\sim 45^\circ$. Dotted lines drawn to corresponding EDPs (c,d) assist the measurement. EDP in (d) is related to EDP in (c) by 180° rotation around the (101)-plane normal, which corresponds to (101) twin operation. The inset shows an SEM image of a similar twin cluster. (b) Second generation of branching follows the same crystallographic rules. Squares indicate the locations of selected area EDPs in (c–f). Colored dots represent simulated diffraction patterns for: R_1 –primary crystal, R_2 –1st generation twin, R_3 and R_4 –2nd generation twins. Small angular dispersion of diffraction spots stems from lateral dispersion of c-axes caused by imperfect fiber attachment. The sample was synthesized using 56 mM Ti(IV)-butoxide in 4.4 M HCl and HT treated at 180°C for 1 hour.

OH^- (hydroxo) groups, which are readily generated through dissociation of H_2O , whereas leaving OR^- ligands are protonated to form ROH (alcohol)^{53,56}. Having 6 bonding orbitals available, Ti^{4+} is prone to form octahedral complexes with ligands⁵². With equatorial orbitals occupied by strongly nucleophilic OH^- ligands, the two axial orbitals remain available as acceptors for bonding weak nucleophiles, such as OH_2 (aquo) in aqueous solutions. Water molecules donate their electron pair towards the empty orbitals of fully positively charged Ti^{4+} , whereby its coordination number is increased from four to six, forming a neutral hydroxo-aquo $[\text{Ti}(\text{OH})_4(\text{OH}_2)_2]^0$ complex. Under supersaturation conditions, neutral complexes are readily attracted by van der Waals forces, and with no repulsion forces involved, they are unstable and aggregate in form of amorphous titania^{53,54,56}. In order to form crystalline products, spontaneous condensation must be avoided. This is accomplished by increasing the acidity of reactant medium^{50,55}. The acid has a dual role; it reduces the initial concentration of dissociated hydroxyl groups $c[\text{OH}^-]$ in the solution (see Supporting Information; Table S1) and protonates OH^- ligands in Ti-hydroxo complex, which increases electrostatic repulsion between the complexes and prevents their immediate condensation^{50,53}. The degree of protonation is governed by the shift of the hydrolysis equilibrium and increases with acidity forming series of positively charged protonated $[\text{Ti}(\text{OH})_{4-n}(\text{OH}_2)_{2+n}]^{n+}$ $|_{n=1,2,3}$ complexes^{54,57}.

Positively charged complexes are repelled from each other and they are stable in suspension until the temperature is increased⁵⁸. With thermal agitation, the complexes acquire kinetic energy that is necessary to overcome electrostatic repulsion forces and facilitate their aggregation via condensation reactions that bind hydroxylated assemblies into oxide structures through the removal of H_2O . In the first step aquo ligands are removed by oxolation process, producing chains of octahedra. This is followed by oxolation, that replaces the remaining hydroxyl ligands by oxo-bridges and combines the chains into a 3D crystal structure^{50,54}. The acidity of the medium thus controls the magnitude of repulsion forces through protonation of Ti-complexes; if complexes with higher positive charge are involved in condensation, they will be spontaneously repelled into more stable linear edge-shared configuration, characteristic of rutile⁵³. Because of strong repulsion between the protonated complexes, angular configurations, such as characteristic for anatase structure are thus not stable under highly acidic conditions. The oxolation reaction combines linear chains of Ti-octahedra into 3D rutile fibers that gradually condensate from the precursor gel (see Supporting Information; Figure S3). During condensation, the positive charge of

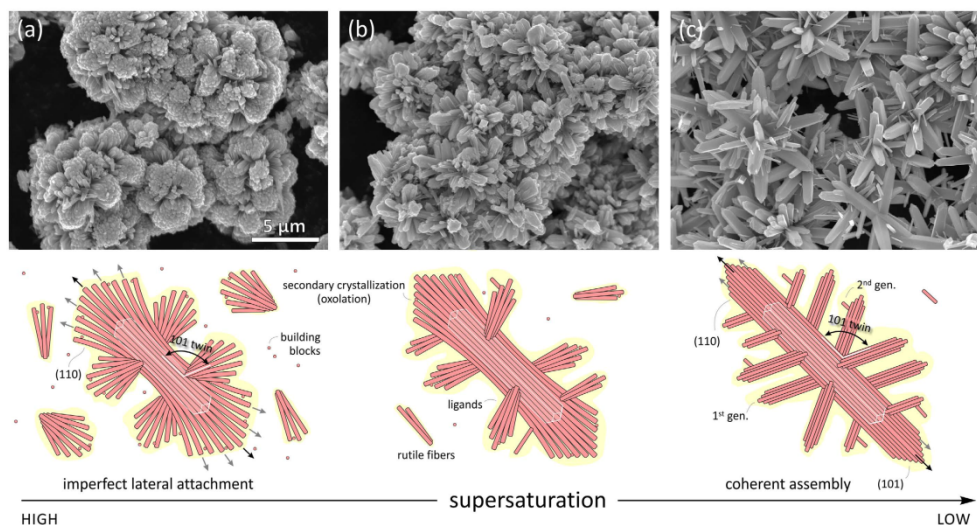


Figure 6. The effect of precursor concentration of the morphology of the product. (a) Under high supersaturation conditions (*i.e.* high precursor concentration; 83 mM of Ti(IV)-butoxide), bundles of radiating rutile crystals are formed, producing spherulitic particles. Each bundle is composed of minute rutile crystals twisted few degrees away from the common *c*-axis, whereas individual bundles in such a cluster appear to be linked by twinning. (b) With decreasing supersaturation (56 mM of Ti(IV)-butoxide) the alignment between the rutile becomes more perfect while their length increases. (c) On even further decrease of supersaturation (28 mM of Ti(IV)-butoxide) well-defined multilevel branched crystals of rutile are assembled through perfect lateral assembly and twinning. The samples were synthesized using 4.4 M HCl and HT treated at 180 °C for 3 hours. Illustrations show rutile clusters developed at various degrees of supersaturation.

the polycondensate gradually increases with the length of the chains, which prevents further condensation on the account of increasing partial charge of hydroxo ligands (δ_{OH^-}), which loose their nucleophilic power (*see* Supporting Information; Table S2)^{50,54}. At this point, condensation would therefore be stopped unless aquo ligands are deprotonated.

For deprotonation to take place we need highly electronegative species that strongly attract protons. In our system, such species are Cl^- ions that are abundantly present in the solution through dissociation of HCl⁵⁹. In polar protic solvents like water, chlorine ions are preferably protonated, rather than coordinating highly charged cation⁵⁴. For this reason it does not appear likely for them to conform a coordination polyhedron with Ti^{4+} . Our EDS analysis showed that chlorine is not incorporated into the Ti-polycondensate structures, which indicates that Cl^- ions do not bond to Ti-cation, but they may play some indirect role in condensation. Because of the highly positive charge of protonated polycondensates, Cl^- ions would be drawn towards the positively charged OH_2 ligands (*see* Supporting Information; Table S2). Deprotonation events most probably take place during intramolecular proton transfer⁵⁷, when Cl^- ions can trap the migrating protons. This reduces the increasingly positive charge of the polycondensate and allows further associative reactions and removal of OH^- ligands. In this way, HCl plays the role of catalyst where it: (i) enters the process through protonation of complexes during the hydrolysis of Ti(IV)-butoxide (δ_{OH^-} increases due to protonation), and (ii) departs the process via Cl^- assisted deprotonation of highly charged polycondensates (δ_{OH^-} approaches an asymptotic level where further condensation is sustained). The catalytic function of HCl is illustrated in Fig. 7.

It is reasonable to assume that starting from their nucleation, the chains would propagate in both directions. As a result, in the central part of the polycondensate oxolation can already start, while on its terminations, oxolation is still under way. Ratio between the oxolation and oxolation reactions defines the length of the rutile fibers – under highly acidic conditions long chains of highly protonated Ti-complexes are formed and oxolation is slowed down due to a high number of OH_2 ligands on their surface and as a result long rutile fibers are formed, on the other hand, if the chains are less protonated, oxolation occurs sooner leading to formation of rutile with rod-like morphology. Similar observations were reported by many researchers^{16,17,29,36}. The acidity therefore does not only decelerate condensation⁵⁰, but also determines the balance between the two associative processes, *i.e.* oxolation and oxolation reactions that control the equilibrium shape of precipitates^{36,51}.

Fiber assembly. From the point, when the precipitates reach their equilibrium size they become basic building blocks for assembly of macroscopic mesocrystals through attractive van der Waals forces^{3,4}. Compared to oxolation and oxolation reactions, that produce structurally flawless nanocrystals, this associative process is far less perfect (*see* Fig. 4). Although assembled in almost perfect orientation, the interfaces between the constituent blocks are generally incoherent. The main cause of imperfections lies in the fact that their assembly is not driven

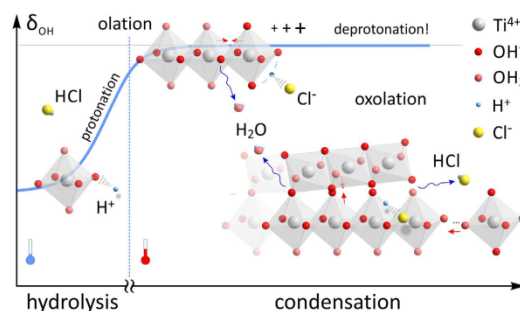


Figure 7. Catalytic role of HCl during hydrolysis and condensation processes. In acidic medium, HCl protonates OH[−] ligands in Ti(IV)-complexes, making them stable at ambient conditions. At elevated temperatures the hydroxo-aquo complexes loose water through associative nucleophilic reactions to form chains of Ti-octahedra (ololation). With their length charge increases to the point when free Cl[−] ions can trap migrating protons and deprotonate growing polycondensate, allowing further release of water (oxolation) and their assembly into the rutile structure.

by chemical (atomic), but rather physical (bulk) interactions. These interactions depend on crystal size, habit, intrinsic electrostatic and magnetic fields, polarization, capping ligands, solvents, particle agitation, *etc.*, and their cumulative effect that leads to oriented attachment remains largely unexplored^{8,49}. Given the complexity of interactions it is astonishing how elementary particles aggregated in mesocrystal assemblies so closely mimic the structure of single crystals^{4,5,13}.

What are the forces that align the nanoparticles? While many authors suggest that either dipolar interactions or intrinsic electric fields are responsible for oriented attachment^{3,4,11,12,60}, the most recent review on self-assembly of mesocrystals concludes that the nature of these forces is still unknown⁴⁹. Using molecular-dynamics (MD) simulations, Fichthorn⁶¹ demonstrated that in vacuum anatase crystals are aligned in accordance to their electric fields rather than due to dipolar interactions, whereas in aqueous medium interactions become more complex. Due to repulsion forces of capping ligands on their surface, nanoparticles were found to explore many possible configurations within the interacting electric fields, before they are finally attached. In this process, many transient bonds are formed and broken, if configuration is energetically unstable. When the crystals are finally met in low energy configuration, they are further attracted by interacting crystal fields and fastened in position by hydrogen bonds. In this state, dehydration reactions take place and more stable oxygen bonds are formed in a zipper-like mechanism that closes down the interparticle gap and fixes the crystals in particular orientation. This theoretical study is in many ways consistent with our experimental observations. In our study we provide an experimental evidence of the existence of such envelope of ligands and mineralizing complexes that assist crystallization of nanoparticles through condensation reactions in form of ~1 nm thick amorphous layers surrounding the rutile fibers (Fig. 4). Their width is comparable to adsorption thickness of solvent molecules reported for rutile based on MD simulations and x-ray photoelectron spectroscopy^{62,63}. High sensitivity to electron irradiation suggests that the surface structure of mesocrystalline rutile is electronically unstable due to unsatisfied bonds¹⁰. In addition to surface amorphous layers we find, enclosed by imperfectly assembled rutile fibers, pockets of amorphous material that are indicative for mesocrystal formation^{3,4}. Within these pockets complexes in loosely associated state are organized in semi-periodic manner. Although not forming a discrete structure yet, building blocks (*i.e.* complexes with ligands) show harmonic order that appears to be induced by interplanar spacing of the constraining lattices. The existence of force fields that assist crystallization in a way that building blocks enter the crystal field in an organized manner, before forming chemical bonds, has already been documented in literature. For example, when studying the interface between Al₂O₃ and liquid aluminum, Oh *et al.*⁶⁴ observed an interesting phenomenon of ordering in amorphous Al induced by the parent crystal structure. They showed that this ordering propagates up to 6 monolayers into the liquid, which is a similar extent as that observed in our study (Fig. 4). In our case the amorphous material is not a liquid, but a gel-like assembly of charged complexes⁶⁵, which are organized following the underlying crystal structure. The observed harmonic ordering of amorphous material may reflect a frozen state of yet unexplained force fields⁴⁹, that may be the key process of conveying the essential structural information between the particles across a thick protective cloud of ligands and poorly ordered unreacted complexes.

When the particles are in movement (by thermal agitation) their electromagnetic fields are coupled⁵⁴, and the particles are aligned parallel to their long axis. Due to multiplicity of interactions the particles are attracted into a loosely associated state^{61,66}. As the distance between the fibers becomes shorter, by attraction, crystallographic alignment along the lowest energy {110} planes becomes dominant⁵¹. Oriented assembly of rutile fibers into bundles is observed already in early stages of synthesis (Fig. 3a). With time, the gap between the fibers is closing down (Fig. 3c) until the fibers are packed in highly oriented manner. Elimination of ligands is the last of all processes that finally reduces the overall energy between the two particles^{4,9,10}. In this process, the rutile fibers are merged into a nearly perfect crystal structure, with occasional faults running parallel to {110} planes that witness of the

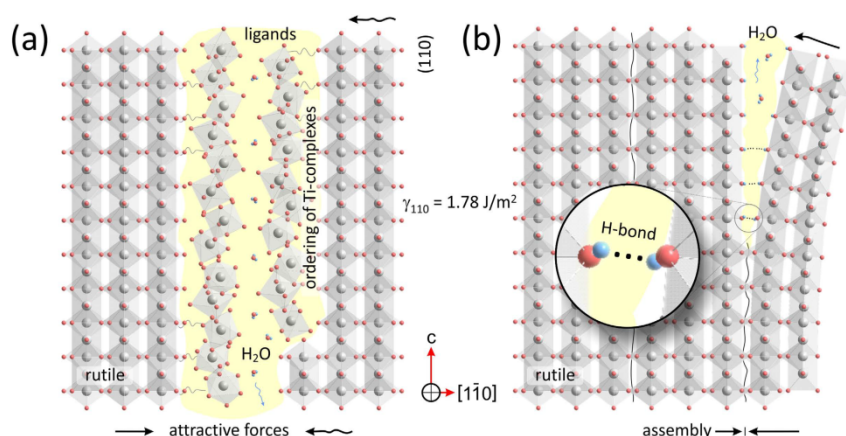


Figure 8. Illustration of lateral fiber assembly along {110} planes of rutile. (a) Precipitated rutile fibers are brought into near-crystallographic orientation by the long-range electromagnetic force field that conveys the essential structural information across a thick protective cloud of poorly ordered ligands and unreacted complexes. The force-field induces harmonic ordering of complexes before they are built into the crystal structure. Ligands and complexes adsorbed on the surface of nanoparticles prevent immediate aggregation, allowing the nanoparticles to explore many possible configurations within the interacting electric fields before they are finally attached. When the distance between the fibers becomes shorter, crystallographic alignment along the lowest energy {110} planes (Oliver *et al.*)⁵¹ becomes dominant. This is followed by elimination of ligands, which finally reduces the overall energy between the two particles. (b) Particles are fastened in a position by hydrogen bonds followed by the dehydration reactions, where more stable oxygen bonds are formed in a zipper-like mechanism that closes down the interparticle gap and fixes the crystals in lateral orientation.

existence of former fibers (Fig. 4). As the nanocrystal assemblies grow larger, further attachments to the existing bundles occur at faster rate. This reduces the chances of perfect alignment with the rest of the bundle. Through continuous condensation of ligands captured in the interparticle space the particles are fixed in accordance to its intrinsic electric field¹¹. As a consequence, crystals acquire twisted morphology, which still follows the symmetry rules of the crystal structure but with angular dispersion (*see* illustrations in Fig. 6; and Supporting Information, Figure S1). This kind of twisting appears to be the main macroscopic evidence of mesocrystal assembly^{3,4}. The described mechanism of {110} lateral attachment of rutile fibers is illustrated in Fig. 8.

Crystal branching (twinning). In literature, twinning in rutile has been attributed to either oriented attachment^{18,19,40,49}, topotaxial replacement reactions^{46–48}, or deformation⁴⁷. To produce twins by mechanical deformation rutile crystals must be subjected to a considerable compressive stress of $> 100 \text{ MN/m}^2$ at elevated temperatures ($> 400^\circ\text{C}$) that generates the necessary energy to activate slip systems to move dislocations⁶⁷. Under HT conditions, where the crystals grow unrestrained, deformation-induced twinning can thus be excluded. For replacement reaction to take place we would need a crystalline precursor phase with structurally related sublattice that is transformed into rutile^{46–48}. Indeed, under some synthesis conditions, the twins have a single nucleation point, suggesting that they form during nucleation of rutile^{40,43–45}. Under our experimental conditions the first precipitate is fibrous rutile with amorphous titania and minor anatase. While anatase and rutile have no 3D structural relation, they are polymorphs of the same compound and participation of anatase in rutile twinning cannot be entirely ruled out.

We confirmed the presence of transient anatase phase after short synthesis times that disappeared in continued HT treatment. The presence of anatase in the initial stages of rutile precipitation is consistent with observations of other researchers¹⁹, and can be explained by a rapid condensation and abundant nucleation after short processing times at low temperatures⁵⁴. As soon as the temperature increases or the time of thermal treatment is extended, anatase nuclei dissolve and recrystallize to rutile. Conditions for the formation of anatase are met at the beginning of HT treatment, when the target temperature is not yet achieved and the concentration of complexes is high. Interestingly, anatase nanocrystals are clustering independently of rutile into their own mesocrystalline assemblies⁶⁸, indicating that a similar physically driven oriented attachment mechanism controls assembly of anatase nanoparticles, as described above for rutile. At elevated temperatures, where supersaturation is lower², and thermally driven kinetic energy of the particles is larger, anatase becomes unstable and disintegrates⁵⁴. In HT medium, anatase probably does not disintegrate into simple ions that would take part in coarsening of rutile through Ostwald's ripening mechanism but is rather protonated (repulsion!) to form elementary building blocks that then, assisted by thermal agitation, rearrange into rutile. Based on the presence of this transient anatase phase, Li *et al.*¹⁹ inferred that twinning of rutile is mediated by anatase-to-rutile transformation. In our TEM

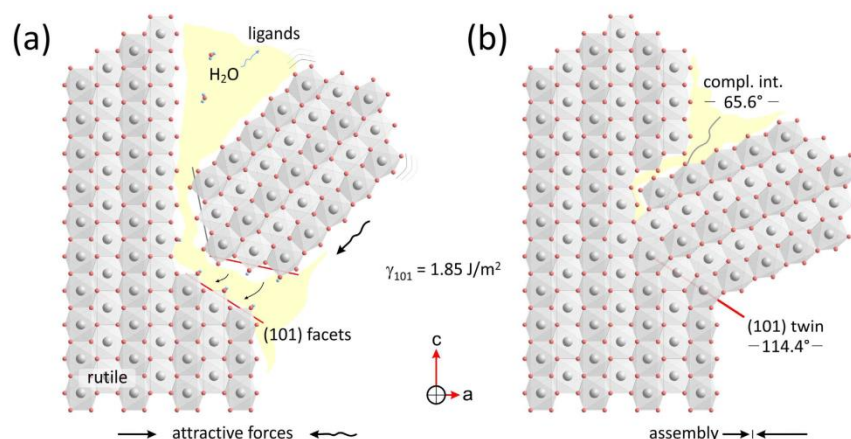


Figure 9. Illustration of twin assembly along {101} planes of rutile. (a) After Oliver *et al.*⁵¹ the {101} are the planes with the second lowest surface energy in rutile. Like {110} planes these can also serve for oriented attachment of suitably oriented rutile fibers. First, the two fibers are brought into near-crystallographic orientation by the attractive electromagnetic forces. This process is likely to take place on surface steps or terminations, where {101} facets are exposed. Unlike lateral attachment this assembly mode brings the two crystals into a {101} twin orientation, that represents one of the lowest energy configurations for rutile. (b) This is followed by the ligand elimination via dehydration reactions, which fixes the fibers in {101} twin orientation with characteristic angle of 114.4° between the c-axis, and its complementary at 65.6°.

investigation we could not confirm any epitaxial relationship between the two polymorphs under employed HT conditions.

Under our synthesis conditions, twinning can occur at any time during growth of rutile, producing branched structures (Fig. 5). As the twinned crystals are not in exact crystallographic relation with respect to the general orientation of the primary crystal (see Fig. 6), their origin must be related to imperfect oriented attachment^{40,49}. Our observations imply that lower is the surface energy of the specific crystallographic face, higher is the affinity for its oriented attachment. Based on calculated surface energies for rutile by Oliver *et al.*⁵¹, {110} faces have the lowest energy, followed by {101} and {001} surfaces. If attachment on {110} planes leads to lateral assembly of rutile crystals, their attachment on {101} planes leads to twinning. Because of slightly larger surface energy and smaller surface area of {101} surfaces, twinning incidences are less frequent than {110} attachment of fibers. They appear to form by oriented attachment of single fibers on {101} steps of rutile bundles at any stage of mesocrystal aggregation. As soon as a fiber is attached in twin orientation, it starts to attract other fibers through lateral attachment. All attachment events are crystallographically imperfect and the interfaces are incoherent. In morphological study of branching in rutile Huang *et al.*²⁰, pointed out that twins are not firmly attached (easily broken off) indicating their imperfect attachment. In addition to {101} twins no other type of twinning is present, except for complementary boundaries⁴⁸, that are produced by impingement of rutile domains in {101} twin orientation. Multiple twinning results in tree-like branched morphology. Because twinning occurs throughout the assembly process, we can obtain fractal-like multi-branched structures, with several generations of twinning. The described mechanism of {101} twin attachment of rutile fibers is illustrated in Fig. 9.

In summary, we provide experimental evidence of theoretically predicted electric force fields that control oriented attachment of crystals. We have shown that multilevel twinned TiO₂ structures are produced by mesocrystal assembly following two sets of low-energy planes {110} and {101} where the degree of branching can be controlled by the choice of experimental conditions. These two self-assembly mechanisms provide the protocol for tailoring desirable 3D branched TiO₂-based architectures.

Methods

Hydrothermal Synthesis. Rutile-type TiO₂ was synthesized following the procedure reported by Zhou *et al.*¹⁶ which produces most versatile branched structures. To study the role of precursor concentration and the acidity of the reactant medium on aggregation and branching of crystals, chosen amount of titanium (IV) butoxide (Ti(IV)-butoxide; 97% Sigma-Aldrich) was added dropwise into 4.4 or 5.5 M aqueous solutions of hydrochloric acid (HCl; 37% Sigma-Aldrich) and mixed until the solution was completely clear. Calculated to the total volume, precursor concentrations varied from 83–28 mM. The resulting solution was used for the proton nuclear magnetic resonance (¹H-NMR) analysis. Additionally, for the unambiguous confirmation of our results we prepared a mixture of n-butanol (99% Alfa Aesar) in 4.4 HCl following the same procedure. The concentration of n-butanol was set to 223 mM, which corresponds to the concentration of n-butanol released in the solution after complete hydrolysis of 56 mM Ti(IV)-butoxide. For hydrothermal (HT) treatment, 2/5 of 23 ml Teflon-lined stainless steel autoclave (Model 4749, Parr Instrument Company) was filled with the resulting solution and heated

at different target temperatures (140–180 °C) and times (0.5–10 h). In our experiments the autoclaves with reagent mixtures were put into the preheated oven. After HT processing the autoclave was cooled to a room temperature and white precipitate from the solution was collected, centrifuged, washed in an absolute ethanol and dried in air. Under extremely acidic conditions and short synthesis times, where the amount of obtained precipitate was low, HCl was first evaporated and then the product was washed in absolute ethanol and dried.

Materials Characterization. Analysis of the starting solution before HT treatment was performed with ^1H -NMR (300 MHz Agilent-Varian) spectrometer, with the use of 5 mm Wilmad[®] NMR sample tubes. Chemical shifts (δ) are reported with respect to TMS. Deuterium oxide (D_2O ; 100 at% Armar Chemicals) in coaxial inset was used as external lock. Phase composition and crystallinity of HT grown products were analyzed by powder X-ray diffraction (XRD) analysis (PANalytical X'Pert High-Resolution PRO diffractometer). The morphology of synthesized branched TiO_2 crystals was subsequently studied using a field-emission scanning electron microscope (FEG-SEM; model Supra[™] 3VP, Carl Zeiss). Based on their morphological features samples were selected for further studies of aggregation and twinning by transmission electron microscopy (TEM; model JEM 2100, Jeol Ltd., Tokyo, Japan), employing selected area electron diffraction (SAED) and high-resolution (HRTEM) techniques that enable an insight into the fine structural features of branched rutile crystals. The samples for TEM studies were prepared by suspending the product in an absolute ethanol and depositing a drop of the fine fraction on lacey carbon coated TEM grids and dried in air before observation.

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Author Contributions

V.J. designed the experiments and optimized the synthesis conditions for growing multiply branched rutile structures. U.J. and J.P. performed ¹H-NMR analysis and confirmed that hydrolysis takes place spontaneously. A.P. initiated the idea of producing multilevel branched inorganic structures for highly selective sensor and separation applications. V.J. and A.R. interpreted the observed lateral and twin based self-assembly mechanisms and wrote the manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

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Chapter 4

Material's Design Beyond Lateral Attachment: Twin-Controlled Spatial Branching of Rutile TiO_2

In this Chapter, we deal with the problem of controlled formation of twins that are the key element of rutile branching. First, the identified assembly modes of rutile together with variation in supersaturation were exploited in order to gain control over OA and twinning. We used rutile crystals as seeds to study the OA and growth in a subsequent HT process. As a follow up of our previous study, where we have shown that twinning is not accidental as speculated by many authors, these results revealed that angular branching is induced and controlled by equilibrium crystal shape (ECS) and electrostatic repulsion among precipitated rutile nanocrystals, which are elementary building blocks, to form 3D branched mesostructures.

We found that the main parameter that decisively influences branching of the products is the acidity of the reactive solution, where high acidity (> 4.4 M HCl) leads to the growth by the classical crystal growth mechanism, and no OA is observed (Figure 4.1, regime I), medium acidity (0.75 M – 4.4 M HCl) initiates both normal growth as well as lateral assembly of precipitates on $\{110\}$ crystal planes (Figure 4.1, regime II), whereas even lower acidity (< 0.75 M HCl) in addition to already observed crystal growth modes also leads to twin assembly along $\{101\}$ crystal planes, *i.e.* spatially branched mesocrystals are produced (Figure 4.1, regime III). The origin of these three growth modes arises from the fact that aspect ratio (l/w , where l is length and w is width) of precipitated nanocrystals linearly decreased by the decrease of acidity (Figure 4.1). Accordingly, high acidity produces long fibrous crystals ($l/w > 12$) that do not assemble and normal growth along high surface energy planes of rutile is dominating the process, while the decrease in acidity produces prismatic nanocrystals ($3 < l/w < 12$) that assemble laterally, and with further decrease of acidity the length of rutile nanocrystals shortens ($l/w < 3$) and initiates their assembly in twin orientation, respectively.

The results showed that the aspect ratio between the prism and pyramidal surfaces of precipitated nanocrystals plays a crucial role in twin incidents, needed to generate the desired branching. By utilization of the observed growth regimes we are able to tune the conditions for controlled OA of precipitates in $\{101\}$ twin orientations, and the frequency of branching is proportionally increasing with precursor (titanium(IV) butoxide) concentration.

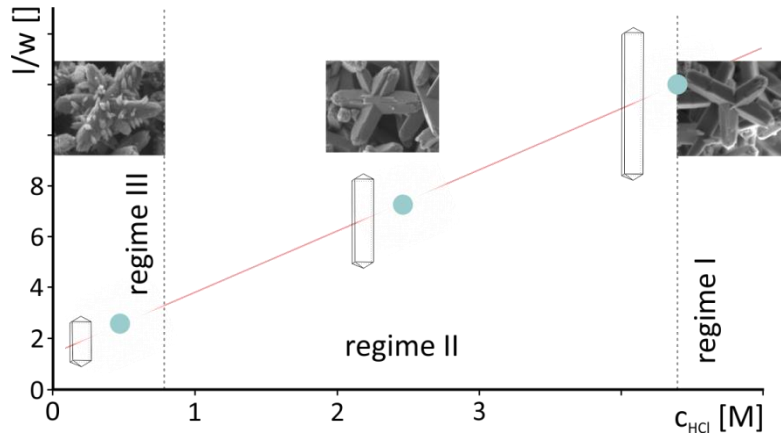


Figure 4.1: l/w aspect ratio of precipitated rutile nanocrystals as a function of medium acidity increase. Three characteristic growth regimes are indicated by dashed lines at 0.75 M HCl and 4.4 M HCl.

During this study we encountered the necessity of defining a simple measure by which we could characterize and quantify branching effects. To evaluate and compare branching and the related increase of specific surface area (SSA) among different nanoparticles, we defined a new criterion, morphology factor (f_m), which is sensitive to particle's morphology, independently of their size. This criterion was inspired by Wadell (1935)[215] in the early 1900's, who defined sphericity (Ψ) as the extent of particle's shape deviation from a perfect sphere. Until today, no simple, generally applicable criterion to characterize diverse morphologies of nanoparticles was available. f_m is a dimensionless parameter, inversely proportional to Ψ and defined as the ratio between effective SSA of the investigated particle (S) and that of an equivalent sphere (S_0):

$$f_m = \Psi^{-1} = \frac{S}{S_0} \quad (4.1)$$

A great advantage of f_m is that it is generally applicable and for the first time we provide a quantitative measure of morphology of any type of nanoparticles that will find many uses in differentiating among structurally and morphologically different materials. Using f_m , it was shown that given a very small volume of secondary twins (5 %), they contribute as much as 34 % of the total SSA increase, whereas the rest is a result of lateral OA of nano-precipitates and porosity induced by classical fibrous crystal growth along high-energy $\{001\}$ planes of rutile. More on this topic is provided in the article entitled "Material's design beyond lateral attachment: Twin-controlled spatial branching of rutile TiO₂", written by V. Jordan, V.D.B.C. Dasireddy, B. Likozar, A. Podgornik and A. Rečnik [216]. Article is presented on the page 53, and it's Supporting Information under Appendix B.

Material's Design beyond Lateral Attachment: Twin-Controlled Spatial Branching of Rutile TiO_2

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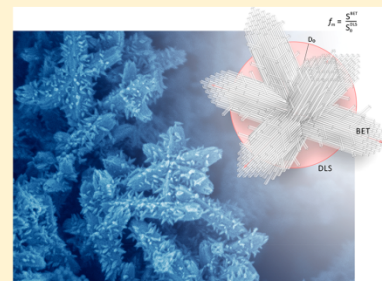
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Supporting Information

ABSTRACT: Crystallization by oriented attachment (OA) is changing our conventional understanding of crystal growth and holds promise for creative design of diverse hierarchic mesostructures. To achieve angular branching of mesostructures, we can exploit twinning. Here we show that in rutile TiO_2 twin-based OA can be realized in a solvothermal process from Ti(IV) -butoxide under mild acidic conditions that favor precipitation of rutile with short-prismatic morphology. The aspect ratio of precipitated nanocrystals was shown to decrease linearly with the acidity of the medium; i.e., lower it is, higher is the affinity for twin OA. For a given aspect ratio, the frequency of twinning is controlled by precursor concentration. Through the control of lateral $\{110\}$ and twin $\{101\}$ OA in rutile, we are able to generate diverse fractal-like multiply twinned inorganic mesostructures for nanotechnology applications. To quantify branching, we define a morphology factor, f_m , a new generally applicable criterion, which provides a quantitative measure of nanoparticle morphology and can be used to evaluate and compare a relative increase of specific surface area for any branched materials.



INTRODUCTION

Ever since Penn and Banfield reported on oriented attachment (OA) of anatase nanocrystals in 1998,¹ great efforts have been devoted to its understanding. Contrary to classical theory of crystal growth,² OA is based on spontaneous oriented assembly of primary nanocrystals producing highly organized mesocrystalline structures³ with more complexity. Different from random aggregation, here the nanocrystals, that are formed by the classical crystal growth mechanism, realign to find a near perfect common lattice orientation and merge to form hierarchic structures along low-index, energetically favored, crystallographic planes.^{3–7} Such self-assembled mesostructures display unique properties, superior to those of nanoparticles or bulk materials, owing to hierarchic alignment of subunits with an increased surface area and high connectivity among the nanocrystalline subunits.^{8,9} Accordingly, the mesocrystals show unprecedented performance in photocatalysis,^{10,11} electrode and optoelectronic materials,^{12,13} as well as in biomedicine,^{8,9} adsorption,^{14,15} highly selective biomolecular separation processes,^{16,17} etc. Until the present day, various solvothermal approaches for the production of mesostructures^{3,9} have been explored in a range

of materials, including CaCO_3 ,¹⁸ ZnO ,^{19,20} CdS ,^{21,22} SnO_2 ,^{23,24} PbSe ,^{25,26} hydroxyapatite,^{27,28} TiO_2 ,^{29–33} etc.^{8,34} Among them, TiO_2 -based mesocrystals have attracted much attention in the past couple of years, due to their potential in many fields, including photovoltaic cells,^{35,36} photocatalysis,^{37,38} water-splitting,^{39,40} separation technologies,^{41,42} etc. The multitude of applications arise from their unique properties, including chemical stability, bandgap, electronic structure, morphology, surface structure, ligand chemistry, etc.^{43,44} The surface properties and interconnection of TiO_2 nanocrystals therefore play a key role in tailoring physical properties for target applications. While due to the lack of experimental evidence the driving forces of OA still remain unclear,⁴⁵ it is believed that the reduction of surface energy by elimination of high surface area^{32,46} assisted by the orientation-specific van der Waals attraction forces^{47,48} is the most probable mechanism behind OA of TiO_2 nanocrystals.

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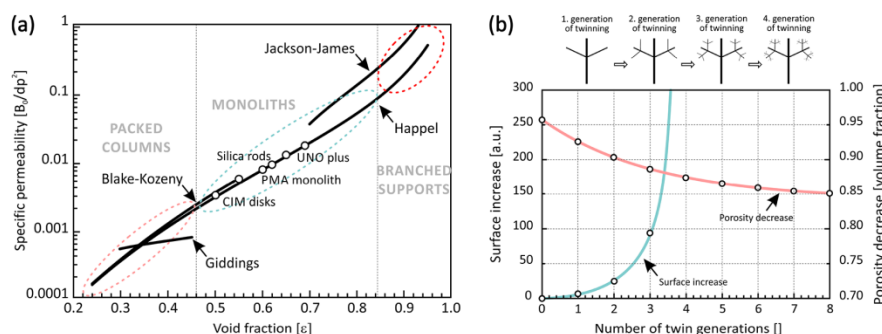


Figure 1. Predicted characteristics of twin-based rutile mesocrystals: (a) specific permeability of conventionally packed columns, monoliths, and twin-based branched supports, adapted after Carta and Jungbauer⁵⁶ and (b) theoretically calculated exponential increase of effective surface area accompanied by a slight decrease in porosity as a function of branching based on twinning in rutile TiO₂ (four twin generations illustrated above). Details of the calculations are available in [Supporting Information](#).

Due to a higher bandgap and superior photocatalytic properties,⁴⁹ the majority of studies on the synthesis and self-assembly of nanocrystalline TiO₂ focus on the production of anatase polymorph of TiO₂.^{32,46} Nevertheless, recently discovered surface properties for hydrothermally synthesized rutile mesocrystals with hydroxylated surfaces show photocatalytic activity matching that of anatase.⁵⁰ Given their more diverse morphologies including rod, spherical, twinned and branched superstructures, that do not form in anatase, it makes rutile superior for applications where high spatial branching and high specific surface area are desired.^{50–53} Among possible morphologies, recently reported hierarchically branched mesostructures based on twinning,⁴⁷ assembled from low-dimensional building units, are of particular interest due to their distinctive functions and novel properties.⁵⁴ One of the numerous applications that would immediately benefit from the controlled synthesis of hierarchically branched mesocrystals based on crystal twinning are separation technologies. Twin-based mesostructures with three-dimensional (3D) fractal branching offer all-scale selectivity and are expected to exhibit by 1 order of magnitude lower pressure drops compared to existing porous supports (Figure 1a). Hypothetically, multiple-generation twinned self-replicating supports could provide an extremely large accessible surface area, required for efficient catalysis but also high binding capacity desirable in chromatography (Figure 1b).⁵⁵ Twin-based branched supports therefore have the potential to solve the current dilemma of having either large pores required for high permeability, or large surface area necessary for high capacity, but not both.

Several mechanisms have been proposed to explain twinning of rutile mesocrystals since the first study by Yang et al. (2009)⁵⁷ who suggested that hydrochloric acid (HCl) acts as a catalyst to induce twinning. Since then, different mechanisms, including topotaxial replacement of anatase, etc., have been reported by other researchers,^{53,58,59} but have never been explained as a mesocrystal assembly process. Just recently we have shown that, under acidic conditions, precipitated rutile fibers self-assemble by OA along two low energy planes, {110} and {101}, where the latter produces the twins.⁴⁷ This mechanism involves shape-specific van der Waals interactions with their spatial extent ranging up to 20 nm, structure-specific electromagnetic interactions <5 nm, completed by hydrogen

bonding and dehydration processes <1 nm, that fix the nanoparticles into a mesocrystal structure. Such long-range direction specific interactions have been now confirmed by environmental transmission electron microscopy–atomic force microscopy (ETEM-AFM) experiments.⁴⁸

If the twinning of rutile is indeed a self-assembly process, it should be possible, hypothetically, to produce multiply twinned, branched crystals, as illustrated in Figure 1b. To verify this hypothesis, we designed experiments to exploit self-assembly for obtaining the desired spatial branching. To initiate growth we resorted to seed mediated hydrothermal (HT) synthesis, where we used rutile seeds as templates for homoepitaxial growth and branching of younger generations of rutile. To characterize steric effects of branching, the products were studied by dynamic light scattering (DLS), specific surface area (SSA) measurements, and electron microscopy methods.

EXPERIMENTAL METHODS

Synthesis. HT Synthesis of Seed Crystals. The seed crystals of rutile with well-defined morphology were obtained following the synthesis route suggested by Tomita et al. (2006)⁶¹ with a few modifications. Briefly, titanium powder (10 mmol 99.5%, PI-KEM Ltd.) was first dissolved in an ice-cooled solution of 10 mL of ammonium hydroxide (NH₃; 25% Merck) and 40 mL of hydrogen peroxide (H₂O₂; 30% Carlo Erba) for 2.5 h. All the chemicals were analytical grade and used without further purification. After dissolution the pH was ~10. After ligand exchange reaction with 27 mmol of glycolic acid (C₂H₄O₃; 99% Sigma-Aldrich) and evaporation at 80 °C for 1.45 h the pH value dropped to ~7. The solution was then held at 70 °C for 19 h and subsequently dissolved in 40 mL of Milli-Q water (pH ≈ 6). Teflon-lined stainless steel (model 4749, Parr Instrument Company, Illinois, USA) batch reactor with 23 mL capacity was used for HT synthesis. The reactor was filled with 9 mL of prepared solution and heated at 200 °C for 24 h. The final mass of obtained TiO₂ seed crystals was ~160 mg. To increase the final amount of TiO₂ crystals for DLS and BET measurements, we used a 97 mL Teflon-lined stainless steel reactor. The reactor was filled with 38 mL of solution and treated under an identical regime as above. After HT processing, the autoclaves were cooled down to a room temperature, and white precipitate from the solution was centrifuged, washed in an absolute ethanol four times, and dried in air at room temperature. The final mass of synthesized TiO₂ crystals was ~690 mg.

Seed-Mediated HT Processing. A subsequent HT synthesis was carried out by mixing 10 mg of initially prepared compact seed

crystals with 9 mL of 0.5–4.4 M hydrochloric acid (HCl; 37% Carlo Erba) directly in 23 mL Teflon cups in an ultrasonic bath (model Sonis 4, Iskra PIO d.o.o., Šentjernej, Slovenia) for 2 min, followed by additional mixing for another 15 min at 600 rpm to achieve complete immersion of the seed crystals. After that, 12.6–25.1 mM of Ti(IV)-butoxide (Sigma-Aldrich 97%) was added dropwise into the suspension and mixed for another 15 min. The suspension was HT treated at 100 °C for 2–24 h. The final mass of obtained TiO₂ mesocrystals in 0.5 M aqueous HCl varied from ~16 mg when using 12.6 mM Ti(IV)-butoxide, to ~20 mg and ~26 mg, when using 18.9 mM or 25.1 mM of Ti(IV)-butoxide, respectively. For DLS and BET analyses where the total amount of the product must be larger, HT synthesis was scaled-up. Here, 44.4 mg of seed crystals was dispersed in 39.9 mL of 0.5 M HCl aqueous solution directly in a 102 mL Teflon cups by an ultrasonic bath for 8 min, and then mixed for another 15 min at 400 rpm. After homogenization, Ti(IV)-butoxide was added dropwise into suspension to achieve concentration of 12.6 mM and mixed for another 15 min. The suspension was HT treated at 100 °C for 4 h. After HT processing, the autoclaves were cooled to ~30 °C, and white precipitate from the solution was collected, centrifuged, washed in an absolute ethanol four times, and dried in air at room temperature. The final mass of obtained TiO₂ mesocrystals increased proportionally with the amount of added seed crystals to ~70 mg per batch.

Characterization Methods. X-ray Diffraction (XRD) Analysis.

Phase composition of the samples was characterized by powder X-ray diffractometry (PANalytical X'Pert High-Resolution PRO, Almelo, The Netherlands) with CuK α radiation ($\lambda = 1.5406$ Å) and a fully opened 100 channel X'Celerator detector under a continuous scanning mode in 2θ range from 10° to 80°.

Scanning and Transmission Electron Microscopy (SEM, TEM).

The morphological characteristics of synthesized crystals were first studied using a field-emission scanning electron microscope (FE-SEM; model JSM-7600F, Jeol Ltd., Tokyo, Japan) to select samples for further investigations by transmission electron microscopy (TEM; model JEM 2100, Jeol Ltd., Tokyo, Japan). Selected area electron diffraction (SAED) and high-resolution (HRTEM) techniques were employed to resolve structural features of the synthesized seed and mesocrystals. The samples for TEM studies were prepared by suspending the product in an absolute ethanol and depositing a drop of the fine fraction on lacey carbon coated Ni-grids and dried in air before observation.

Dynamic Light Scattering (DLS). Effective (hydrodynamic) diameter (D_0), a log-normal particle size distribution and polydispersity index (PDI) of commercially available, seed, and mesocrystalline rutile were measured by dynamic light scattering (PALS, ZetaPALS Potential Analyzer, Brookhaven Instruments Ltd., New York, USA) using a scattering angle of 90°, beam wavelength of 658 nm, and a run time of 3.3 min. PDIs of all our samples fall between 0.08 and 0.7, indicating their polydisperse size distribution, specified in the instruction manuals of the instrument, making them suitable for the DLS technique. The collected data were analyzed for the set of experimental parameters (BIC Particle Sizing Software 4.14). For DLS analysis, the samples were suspended in Milli-Q water (0.04 g/L) using an ultrasound bath for 10 min, followed by further sonication using an ultrasonic tip (model Sonics & Materials, Inc., Newtown, USA) for another 3 min. Small aliquots of well dispersed powders were subsequently used for the analysis. The particle's morphology (verified by SEM) was not affected by an ultrasonication procedure. Commercial rutile, manufactured via sulfate processing of ilmenite in Cinkarna Celje d.o.o., Slovenia, was used as a reference sample (Supporting Information, Figure S1).

Specific Surface Area (SSA) Analysis. Specific surface area of the samples was studied using the Brunauer–Emmett–Teller (BET) method. To improve accuracy, 100–300 mg of synthesized materials was used. First, the samples were degassed in N₂ atmosphere for 4 h at 200 °C. SSAs of the degassed samples were then examined by physisorption measurements of N₂ on the sample's surface using Micrometrics ASAP 2020 analyzer. The particle's morphology (examined by SEM) was not affected by the degassing procedure.

RESULTS

In our study primary twinned rutile crystals (first generation) were used as nuclei for mesocrystal growth by lateral and twin (second generation) attachment. The OA process was studied under different HT conditions, i.e., acidity, precursor concentration, temperature, and synthesis time to understand their influence on branching of the mesocrystals. Particle size distribution and morphological features of mesocrystalline rutile (m-rut), initial seed rutile crystals (s-rut), and commercial rutile TiO₂ (c-rut sample), were measured and compared with respect of branching.

Seed Rutile (s-rut). Morphology and phase composition of the primary s-rut crystals is shown in Figure 2. The products

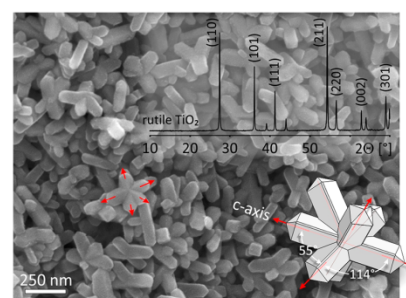


Figure 2. Morphology of seed (s-rut) crystals synthesized by HT oxidation of titanium powder. The product is composed of well-defined rutile nanocrystals (powder XRD overlay) radially extending from common junctions (*c*-axes indicated by red arrows). The crystals enclose angles characteristic of twinning (illustration; bottom right). The crystals are confined by {110} prism and {111} pyramidal planes.

comprise plentiful submicron clusters, composed of short-prismatic rutile crystals that radiate from common junctions. Individual crystals in these clusters have well-defined prism and pyramidal terminations, approaching their equilibrium crystal shape (ECS). All crystals apparently enclose characteristic angles that suggest twinning. The dimensions of the rutile crystals range from 120–230 nm in length (l , along the *c*-axis, measured from the junctions, and are approximately 50–90 nm wide (w ; across the prisms; [110]-direction), resulting in an average l/w ratio of ~2.5.

The observed angular connectivity of the seed rutile crystals, obtained following the synthesis route suggested by Tomita et al. (2006)⁶¹ were to date not sufficiently addressed. To characterize the initial geometry of seed crystals, the finest fraction of the seed rutile's was studied by TEM. The crystals are not randomly intergrown, but appear to be interconnected through twin relations. To confirm the twin relations, the interfaces were studied in low-index zone axes where the boundary between the crystal domains is viewed parallel to the electron beam. The easiest zone axis to determine the twin relations would be [010];^{62,63} however owing to their branching, this zone axis is difficult to obtain as the multipod crystals commonly pin to the carbon TEM foil out-of-plane (see Jordan et al. (2016)⁴⁷). Therefore, we studied the crystals in [111] and [113] projections (Figure 3), where the boundaries are also viewed edge-on, just determination of the twin law is not as straightforward. Using either fast Fourier transform (FFT) across the twin plane, or selected area

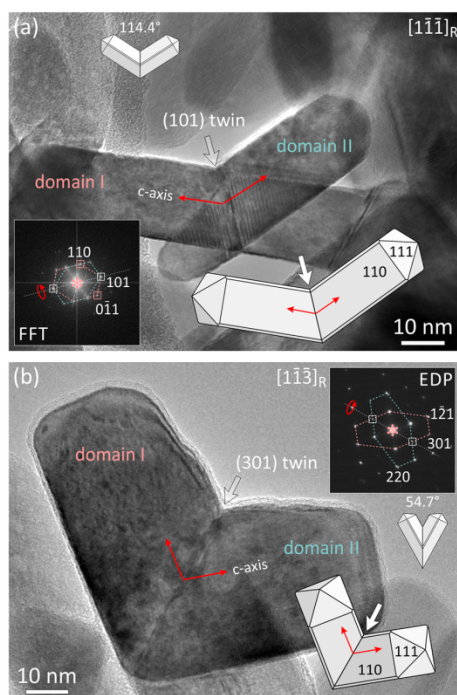


Figure 3. Crystallographic study of HT grown s-rut crystals, displaying two types of twinning: (a) (101) twin viewed in $[111]$ orientation (FFT; bottom left corner) and (b) (301) twin viewed in $[113]$ orientation (SAED; upper right corner) with the characteristic angles of 114.4° and 54.7° between the c -axes (indicated by red arrows). Larger illustrations correspond to the exact crystal orientations as observed by TEM.

electron diffraction (SAED) we could confirm that the crystal clusters are composed of two types of twins, the more common (101) twin⁶² and the less common (301) twin⁶³ with the characteristic angles of 114.4° and 54.7° between the crystallographic c -axes, respectively. Out of 16 possible incidences, s-rut crystals comprise about six crystals in average intergrown in twin orientations, producing the desired initial 3D branching.

Mesocrystalline Rutile (m-rut). Under homogeneous nucleation conditions, a high activation energy has to be overcome for the onset of the crystallization process; therefore, seed crystals were used to lower the nucleation energy and serve as templates for continued (homoepitaxial) growth.² Compared to homogeneous nucleation conditions, the temperature necessary to induce the crystal growth is also lowered under seed mediated growth. s-rut was used to study the OA and growth of rutile TiO₂ in a subsequent HT process. From precursor concentration, synthesis temperature, and HT treatment time, the main parameter that decisively influences phase composition, morphology, and consequently the branching of the products is the acidity of the medium. The acidity plays the key role on the solvent activity and thus effectively controls the ECS of precipitates via condensation reactions.⁶⁴ In the case of rutile, the increase of acid

concentration promotes the olation process and suppresses oxolation, which in effect leads to the formation of fibrous rutile,⁴⁷ whereas lower acidity promotes the growth of short-prismatic rutile crystals. Regardless of their initial crystal shape, any seed crystal, used in the synthesis, will undergo a morphology transition into a thermodynamically more stable shape for the new growth conditions. Under acidic conditions, products develop fibrous morphology (Figure 4a). In this process, seed crystals are overgrown by a new generation of rutile producing characteristic acicular terminations (Figure 4b), resembling those reported previously.^{47,65–68}

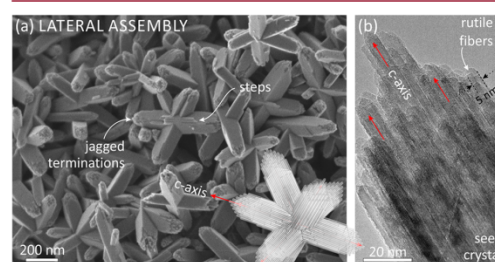


Figure 4. Seed mediated crystallization of rutile in 2.4 M HCl with 25.1 mM Ti(IV)-butoxide HT treated for 24 h at 100°C . (a) The products show steps on prism surfaces resulting from concurrent lateral OA and typical jagged terminations due to homoepitaxial growth of fibrous rutile over implanted seed crystals, precisely shown in (b). The fibrous morphology of the product is illustrated in the lower-right corner of (a).

Under acidic growth conditions, ECS can be more simply represented by the length (l) and width (w) of precipitated rutile fibers that are present in the fine fraction of growth solutions (Supporting Information, Figure S2). Measuring their ratio as a function of acidity shows a simple linear dependence:

$$l/w = 2.41c_{\text{HCl}} + 1.33 \quad (1)$$

as illustrated in Figure 5. Under highly acidic conditions, at 4.4 M HCl, the typical length of the rutile fibers is 50–70 nm, whereas in the 2.4 M HCl the fibers are shorter and measure 30–40 nm. Their width is rather constant and measures from 3 to 7 nm, resulting in l/w aspect ratios of ~ 12 and ~ 7 , respectively. Additional decrease in medium acidity to 0.5 M

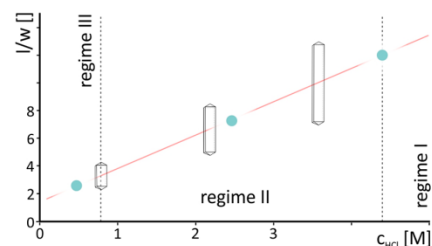


Figure 5. Dependence of l/w aspect ratio on the acidity of the medium (concentration of HCl) spanning over three characteristic growth regimes indicated by dashed lines at 0.75 M HCl and 4.4 M HCl.

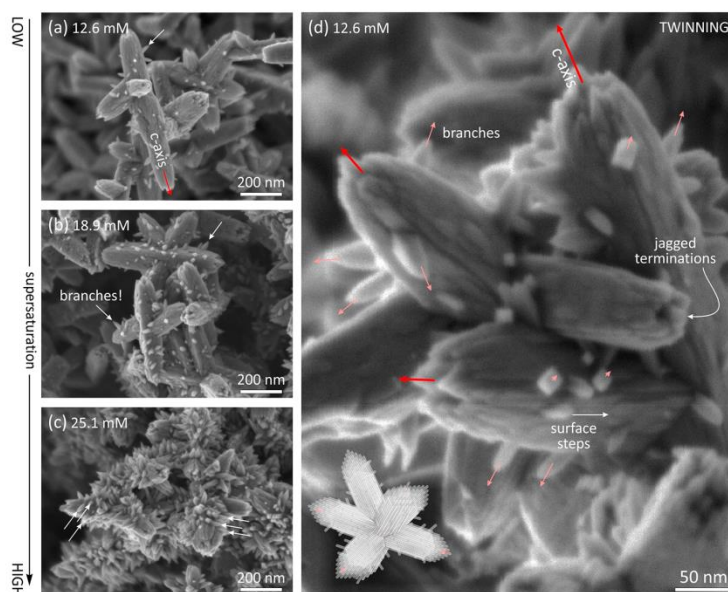


Figure 6. Influence of Ti(IV)-butoxide concentration on the frequency of spatial branching in rutile (HT treated in 0.5 M HCl for 2 h at 100 °C): (a) 12.6 mM – the onset of branching, (b) 18.9 mM – medium branched and (c) 25.1 mM – highly branched mesocrystals. (d) Close-up of branched m-rut crystals, showing numerous newly grown branches and surface steps (illustrated below). Red arrows indicate the directions of *c*-axes of the primary (dark red) and secondary twinned crystals (light red). The characteristic length of the individual branches under these growth conditions (scale-up) is 20–40 nm and their width is 7–15 nm.

HCl further decreases the fiber's length to 20–40 nm, while the width is increased to 7–15 nm, resulting in a lower *l/w* aspect ratio of ~ 2.7 . The intercept at ~ 1.33 in eq 1 (Figure 5) approaches the *l/w* ratio of 1.35 that corresponds to the hypothetical isometric rutile with equal central distances of {110} and {111} planes.

However, the medium acidity defines not only the apparent *l/w* aspect ratio of crystallites but also interparticle repulsion through positively charged ligands on the surface of crystallites that largely determine the controlling growth mechanism.⁴⁷ Depending on the acidity, we observe three characteristic growth regimes: I – high acidity; normal growth, II – medium acidity; lateral OA, self-assembly on {110}, and III – low acidity; twin OA, self-assembly on {101}.

These three growth regimes can be utilized to control the morphology and branching of the final products. Under extremely acidic growth conditions, we observe precipitation of long fibers that do not self-assemble (i.e., regime I).⁶⁶ Using seed crystals as the templates for heterogeneous nucleation, the rutile fibers grow mainly on the pyramidal {111} s-rut terminations, whereas almost no OA can be observed. As the acidity is gradually decreased, the fibers start to attach laterally. Under medium acidic conditions (i.e., regime II), rutile rods with lower *l/w* aspect ratios start to precipitate from the solutions. The growth mechanism is now dominated by accelerated lateral OA. In the case of using seed crystals, OA of precipitated rutile fibers starts to take place on the prism surfaces of s-rut crystals, while fibrous growth on s-rut terminations is sustained (see Figure 4). A further decrease of acidity (i.e., regime III) leads to precipitation of short-

prismatic rutile crystals, showing abundant lateral as well as twin OA.⁴⁷ Above this regime anatase can start to precipitate along with rutile. Lower is the acidity, higher is the fraction of twin incidences, and hypothetically, OA by twinning would prevail over lateral OA as the *l/w* aspect ratio is approaching the value for isometric ECS of rutile. On s-rut, all three regimes are observed—fibrous growth on s-rut terminations (regime I), lateral OA of rutile fibers displayed as surface steps (regime II), and abundant OA by twinning (regime III).

To promote twinning by OA, the medium acidity must therefore be suitably adjusted. When this is achieved, the frequency of spatial branching can be further tailored by tuning the supersaturation conditions. As shown in our recent study of OA in rutile, the precipitation rate can be adjusted either by the increase of precursor concentration or a decrease of HT treatment temperature.⁴⁷ Figure 6a–c shows the effect of precursor concentration on branching of m-rut for chosen growth conditions that promote OA by twinning (0.5 M HCl). In addition to lateral OA, we observe intense branching of m-rut generation. The frequency of branching increases proportionally with precursor concentration. A close-up of the product (Figure 6d) shows an interplay of all three regimes: jagged terminations—a result of normal growth, surface steps—a result of lateral attachment, and numerous branches—produced by twinning. XRD analysis of the products under highest supersaturation conditions (~ 25 mM Ti(IV)-butoxide; Supporting Information, Figure S3a) shows minor amounts of anatase.⁴⁷ On prism faces of m-rut crystals, we often observe small rectangular holes from detachment of

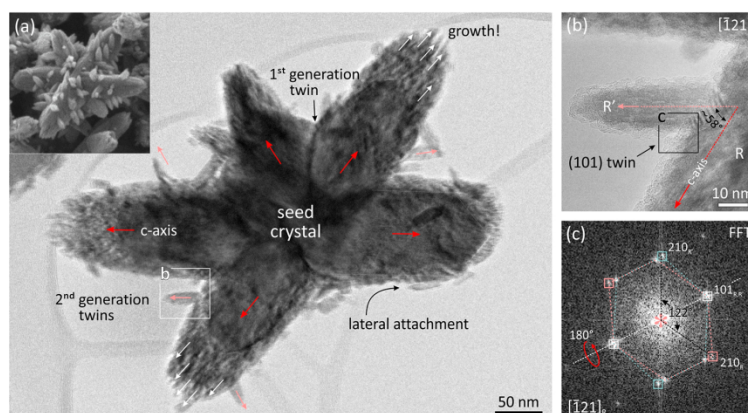


Figure 7. TEM study of 3D branched rutile after subsequent HT treatment of s-rut crystals (18.9 mM Ti(IV)-butoxide in 0.5 M HCl at 100 °C; 2 h). (a) m-rut cluster grown under selected conditions (regime III: fiber overgrowth + lateral + twin OA). Similar cluster is shown in SEM image (see inset in upper-left corner). Red arrows denote the orientation of the *c*-axes in the primary s-rut crystal and secondary branches (light red). (b) Orientation relationship between the primary s-rut and secondary m-rut branch in the $[121]$ zone axis. From the angle of $\sim 58^\circ$ between the (210) lattice planes, that are resolved in this projection, (101)-twin relation is confirmed by (c) FFT from the twin junction (for more details, see Jordan et al. (2016)⁴⁷).

Table 1. Calculated Morphological Factors, f_m for Branched Rutile Particles, Based on Actual SSAs of the Particles, S Measured by BET Method and the SSAs of the Equivalent Spherical Particles, S_0 Measured by DLS (eq 2)^a

branching levels	D_0 (DLS) [nm]	S_0 (DLS) [m ² /g]	S (BET) [m ² /g]	f_m []	f_m' []
c-rut: no twinning	326.0 ± 13.3	4.40 ± 0.12	6.86 ± 0.07	1.56	1.50
s-rut: first twin gen.	225.4 ± 6.8	6.30 ± 0.13	15.80 ± 0.18	2.51	2.26
m-rut: second twin gen. ^b	298.4 ± 22.1	4.80 ± 0.24	25.79 ± 0.36	5.37	3.14

^aFor comparison, f_m' values were calculated from the morphology of the particles as recorded by SEM images (for more details see Supporting Information). ^bScale-up synthesis using 12.6 mM Ti(IV)-butoxide HT treated in 0.5 M HCl for 4 h, 100 °C (the product shown in Figure 6d).

twinned nanorods due to weak assembly forces (Supporting Information, Figure S4).⁶⁹

TEM image of typical branched rutile cluster viewed in the $[121]$ projection is shown in Figure 7. The shape of the primary s-rut crystal can still be discerned under the younger fibrous rutile. In addition to finger-like growth on the terminations of s-rut crystals, lateral OA and formation of small branches can be observed. The growth features and the aspect ratio of the branches are characteristic for low acidic conditions (0.5 M HCl; regime III). Analysis of crystallographic relationships between the primary s-rut and the impinging secondary m-rut crystals (close-up in Figure 7b) confirms they are in twin orientation (FFT in Figure 7c) and that twin-controlled spatial branching is achieved.

Characterization of Branching. For any nanotechnology applications, such as photocatalysis or separation processes, where the effective surface area of nanoparticles is one of the key parameters, more than just a qualitative assessment of branching is needed. In order to properly understand and to evaluate the effects of branching on the specific surface area (SSA) of the products, we performed DLS and BET characterization of the samples. The analysis was done for the commercially available reference sample, denoted as c-rut (no twins; Supporting Information, Figure S1), s-rut crystals (first generation of twinning; Figure 2), and branched, m-rut crystals (second generation of twinning; Figure 6d).

SSA of a spherical particle, S_0 , represents the surface area of the particle, A_0 , per its mass, m ; that is inversely proportional

to its diameter, D_0 , multiplied by its density, ρ (see Supporting Information, eq S4):

$$S_0 = \frac{A_0}{m} = \frac{6}{D_0 \rho} [\text{m}^2/\text{g}] \quad (2)$$

Now, to evaluate the effect of branching among different particles of the same material, we introduce a morphology factor, f_m , that is inversely proportional to the sphericity of the particle, Ψ^{-1} (see Supporting Information, eqs S2–S3),⁷⁰ and is defined as the ratio between effective specific surface area of the particle, S , and that of an equivalent sphere, S_0 , with the identical volume:

$$f_m = \frac{S}{S_0} \quad (3)$$

being 1 for spherical and >1 for nonspherical particles (see examples Supporting Information, Table S1), reaching its maximum for fractal particles.⁷¹ The effective hydrodynamic diameter of the particles is readily measured by DLS, where D_0 is calculated from an equivalent solvated spherical particle, that diffuses similarly as the particles that are being measured. Average D_0 values of our samples were determined from DLS log-normal size distribution graphs (Supporting Information, Figure S5). The corresponding S_0 of equivalent spherical particles is calculated and listed in Table 1. The effective specific surface area S_0 , calculated based on DLS, is then compared to actual specific surface area, S , based on BET

measurements, to obtain the morphology factors, f_m for our samples (Figure 8 and Table 1). f_m is a dimensionless variable

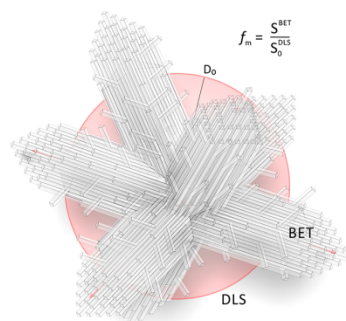


Figure 8. Schematic illustration of branched rutile cluster with two generations of twinning. Morphology factor, f_m , is calculated as a ratio of SSA of the cluster, S , measured by BET vs. SSA of solvated spherical particle, S_0 , with diameter D_0 from DLS measurements.

independent of particle sizes and can be used to compare branching over different length scales. Given its simplicity, f_m can be used as a simple measure of particle branching, roughness, or SSA increase among different products and is generally applicable to any material.

The apparent increase in SSA seems to be significant. In terms of f_m , the first generation of twins as shown by s-rut, compared to rod-like nontwinned crystals of c-rut, produces a 1.6-fold increase of the SSA, whereas for second generation of twins of m-rut particles, the increase is already 3.4-fold. The observed increase follows the predicted trend for fractal twinned rutile, as shown in Figure 1b. To estimate how much of this increase is to be attributed to second generation of twinning and how much to the porosity induced by fibrous growth and lateral OA of mesocrystalline rutile, we calculated f_m' values from SEM images. In this calculation, the base m-rut crystals and twins were assumed to be compact with l and w measured from their geometry (see Supporting Information for details). By this assumption, the effect of porosity is neglected, and only contribution of twinning can be assessed. This shows that even if the volume fraction of the second generation of twins is relatively low (for measured crystal dimensions and details of calculations see Supporting Information, Tables S2–S3), they contribute as much as one-third of the total SSA increase, while the rest of the increase is due to fibrous growth and lateral OA.

DISCUSSION

In the present work, we demonstrate that 3D fractal branching of rutile TiO_2 can be induced by mesocrystal self-assembly through twinning under the low acidity growth conditions. The control of acidity and precursor concentration is critical to achieve the required morphology of precipitates that is necessary to generate the desired branching of the products. Seed crystals were used to achieve more uniform nucleation conditions in hydrothermal batch processing.

We identified the following mechanisms that determine the final morphology of the products: (i) normal crystal growth, (ii) lateral OA, and (iii) OA by twinning. All three processes compete during mesocrystal formation and have distinct

growth features. The first mechanism takes place on the terminations of seed crystals and continues as long as necessary to achieve a new equilibrium shape (ECS) under given synthesis conditions.² On the other hand, seed crystals also serve as a template for oriented attachment of freshly precipitated rutiles. We find that the acidity of the reactive medium is the key parameter to control ECS of precipitates, whereas precursor concentration can be used to tune their frequency. For prismatic morphology, ECS of rutiles can be represented by the l/w ratio that is linearly dependent on acidity (Figure 5). According to Jordan et al. (2016),⁴⁷ the acidity of the medium effectively controls the ratio between two dehydration processes, where the first (olation) promotes linear growth of rutile fibers, while the second (oxolation) is responsible for their lateral growth. We have shown that there exists a straightforward dependence of lateral and twin OA on the aspect ratio of precipitates through olation/oxolation ratio. In extremely high acidic conditions long rutile fibers are formed that do not self-assemble.⁶⁶ Under moderately acidic conditions, long prismatic crystals are formed ($c_{\text{HCl}} > 0.75$), lateral OA is favored, and under lower acidic conditions the crystals become shorter ($c_{\text{HCl}} < 0.75$) and OA by twinning starts to take place. This gives us a simple tool to control the ratio between lateral and twin attachment, and hence to the final branching of rutile. These observations are in agreement with Penn (2004),⁴ who showed that growth via OA is slower when the particles are highly charged, i.e., highly acidic conditions. Together with the corresponding surface energies,⁶⁰ the aspect ratio between prism and pyramidal surfaces plays the key role in the so-called twin incidents that are needed to generate the branching.⁴⁷

A number of experimental studies imply that OA usually takes place under the conditions of ligand-assisted crystallization, when the particles are electrostatically charged.^{5,72–74} While charged capping ligands play an important role in preventing uncontrolled agglomeration of particles by van der Waals forces,⁷⁵ thermal agitation assists their rearrangement into low-energy configurations. Anticipating that induced charges control particle aggregation, some authors suggested that dipolar interactions are responsible for OA.^{3,22,76,77} However, there is a number of centrosymmetric structures, including rutile, that have no permanent dipoles, and yet they are assembled into mesocrystal structures. By electron holography, Simon et al. (2006)⁷⁶ showed that phase-map image of fluorapatite surprisingly well coincides with its growth sectors and suggested that intrinsic electric fields play the key role in mesocrystal assembly. The origin of particle's electric field and the resulting surface polarization when ionized in a medium therefore stems from the inherent crystal structure. In solution, intrinsic electromagnetic fields of nanocrystals are coupled and attracted into a loosely associated state, until they find low energy configuration.^{7,78} Therefore, in the first stage of OA process we are dealing with a multibody problem when fibers are monodispersed and mutual attractions are highly competitive. To avoid this stochastic assembly step, we used seed crystals as convenient objects for initial OA.

To explain twinning in mesocrystalline rutile TiO_2 , many mechanisms have been proposed in the literature. One of them suggested that concentrated HCl acts as a catalyst and a corrosive agent, that is responsible to induce defects on the surface of rutile, triggering the formation of twins.^{57,58} This mechanism reportedly involves corrosion on the surfaces of existing rutile crystals that attracts ions for nucleation of the

side branches and growth via Ostwald's ripening. On the contrary, we observe twinning of rutile fibers already in the initial stage of their precipitation (Supporting Information, Figure S6). Other authors attempted to explain twin formation by topotaxial replacement of anatase. Accordingly, Ding et al. (2010)⁷⁹ suggested that the twins form by OA of anatase on rutile, followed by a subsequent transformation of anatase into rutile in twin orientation. Roca and Leite (2013)⁵³ agreed with the suggested hypothesis as a result of highly inhomogeneous reaction system, while Li et al. (2013)⁵⁹ added that branching occurs by OA of anatase particles on the tip of rutile nanorods in early growth stages, which are subsequently replaced by rutile in parallel or twin orientation, suggesting that the formation of mesocrystalline rutile is mediated by anatase-to-rutile transformation. While we have confirmed that anatase may indeed precipitate from highly supersaturated reaction solutions (Supporting Information, Figure S3a), they are found to form independent clusters or attach to the low-energy {110} planes of rutile⁴⁷ and not the tips of rutile crystals. Unlike what has been suggested by Li et al. (2013),⁵⁹ the anatase particles do not display {103} forms that would allow oriented transformation into rutile, but rather crystallize in a bipyramidal {101} habit,⁸⁰ which has no structural relation with rutile if attached to its exposed faces. A problem of this type of topotaxial replacement is a large discrepancy between the rutile and anatase lattice parameters and not good matching relation between the two structures. Accordingly we find that {101} habit planes of anatase may indeed be attached to the {110} prisms of rutile but with a high angular misfit due to the lack of structural coherency (Supporting Information, Figure S7). Random attachments suggest that mesocrystal assembly is driven by attractive forces acting between the surfaces of nanocrystals, but only when two particles have a matching structure are they further assembled into mesocrystals through short-range interactions and dehydration processes. In one of the latest studies, Huang and Liu (2014)⁶⁹ interpreted the twinning as a result of defect compensation during crystal growth. Contrary to the growth mechanism, they observe that twins are poorly attached to the matrix, which further substantiates that twins are not a result of growth but macromolecular assembly mechanism, driven by van der Waals interactions,⁴⁸ where the nanoparticles are attached by weak electromagnetic forces rather than strong chemical bonding.⁴⁷ Because of their incoherent nature, twins produced by mesocrystal assembly are not crystallographic (i.e., Friedelian) but hybrid twins.^{81,82} Mesocrystal twinning of rutile is manifested under mild acidic conditions when the aspect ratio of precipitates is low (Figure 5). It can take place at any stage of mesocrystal formation. It not only induces desired 3D branching, but also generates a tremendous increase of specific surface area having a great potential for diverse nanotechnology applications. To fix weakly attached twins, annealing of products should be implemented, as suggested by Folger et al. (2017).⁶⁸

In order to evaluate the effect of branching among different nanoparticles, simple comparison of their SSAs does not reflect a realistic picture because of the size effects. Regardless of their morphology, small particles would generally have higher SSA than large ones, and hence we would need particles with the same spatial distribution to evaluate contribution of branching to the total SSA. As this is usually not the case, we propose a dimensionless morphology factor, f_m , that allows us to decipher the differences in particle morphologies across

different length scales. The basic definition of f_m is simple. It is defined as a ratio of SSA of actual particle vs. that of an equivalent spherical particle that diffuses similarly as the particle that is measured. The first can be obtained directly by measuring SSA using the BET method, whereas the second can be calculated from DLS measurements of a corresponding sample (Table 1). Regardless of the particle size, the proposed methodology is sensitive to particle morphology and can be used as a measure of particle branching. Using f_m we show that twinning has a significant influence on the increase of SSA of rutile clusters. Given their small volume fraction (~5%), twins of second generation contribute as much as 34% of the total SSA increase (Supporting Information, Table S2). Twin branches provide large open surfaces that are accessible by convective fluid flow, important for practical applications of such materials for separations or catalysis, as due to the absence of diffusional limitations both processes would be fast increasing productivity.

CONCLUSIONS

In the present study we provide the first experimental evidence that twinning in mesocrystalline rutile is a self-assembly process, that directly depends on the aspect ratio of precipitated nanocrystals. We show that medium acidity has a dual role in mesocrystal assembly; it controls the morphology of the precipitates and plays the key role in diverting among three competing growth mechanisms:

- (i) Normal crystal growth—high acidity ($c_{\text{HCl}} > 4.4 \text{ M}$); fibrous morphology of precipitated rutile crystals with high aspect ratios $l/w > 12$. Under these conditions olation is dominating condensation process. When using seed crystals as templates for heterogeneous nucleation, the rutile fibers grow mainly on the pyramidal terminations, while no OA of rutile precipitates is observed.
- (ii) Lateral OA – medium acidity ($0.75 \text{ M} < c_{\text{HCl}} < 4.4 \text{ M}$); long-prismatic rutile with aspect ratios of $3 < l/w < 12$. In addition to olation, oxolation is becoming a concurrent condensation process. Owing to lower electrostatic repulsion, precipitates start to self-assemble on {110} prism planes. Lateral OA is observed on prism faces of rutile seed crystals. No twinning is observed.
- (iii) Twin OA – low acidity ($c_{\text{HCl}} < 0.75 \text{ M}$); short-prismatic crystals with the aspect ratios $l/w < 3$. Oxolation is precipitation controlling condensation process. In addition to lateral assembly, precipitates start to assemble on {101} planes, producing OA in twin orientations. OA by twinning is observed among the precipitates, as well as on the open surfaces of seed rutile crystals.

Each subsequent mechanism involves the previous ones. The aspect ratio shows linear dependence on medium acidity, and this relation can be used to tailor branching of the final product. To evaluate the effect of particle branching and its overall contribution to the relative increase of specific surface area, we defined the morphology factor that can be used to compare the degree of branching among morphologically different particles. The proposed methodology enables bottom-up engineering of hierarchically organized nanostructures with tailor-made properties for particular application such as energy harvesting, photocatalysis, multifunctional sensors, and macromolecular separations.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b00479.

Described performed calculations for Figure 1b, details on phase composition and morphology of the samples, details on morphology factor derivation and its determination for simple geometric forms (Table S1) and real samples (Tables S2 and S3), DLS measurements (PDF)

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Author Contributions

V.J. designed the experiments and optimized the synthesis conditions needed to generate the branching. V.D.B.C.D. and B.L. performed the SSA measurements by BET analysis. A.P. made calculations of specific surface areas of particles based on SEM images. V.J. and A.R. introduced the morphology factor, interpreted the results, and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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Chapter 5

Low-Temperature Synthesis of Hierarchical Rutile-Type TiO_2 Mesocrystals

Over the years of exploring and experimenting, conventional HT synthesis became very well understood, however one of the main disadvantages of batch processing that still remains are phase homogeneity and controlled morphology of crystals synthesized in the same HT treatment [217]–[220]. Non-reproducible syntheses are especially critical for the self-assembled materials where the growth controlled by the OA is strongly affected by the inhomogeneity of the system [164], [216]. During the HT process local gradients of concentration and temperature are unavoidable. Under such synthesis it is expectable that particles with different properties will appear, depending on the local conditions each particle experiences [218].

In a review published by Tachikawa and Majima (2014) [65], the authors stressed out an important, yet not sufficiently addressed problem concerning mesomaterials' design:

*“Although self-assembly of nanocrystals by utilizing nanoscale attractive forces provides a simple approach for the fabrication of mesocrystals, the **synthesis** procedures are sometimes very **complicated**, and hence, their large-scale applications are limited. A highly **reproducible**, facile synthesis of **mesocrystals** with a controlled shape and size is strongly desirable for fundamental research and **practical applications**.”*

In view of this challenge, knowledge on self-assembly of rutile precipitates obtained through preceding studies (Chapter 3 and 4) was fully applied here. From the application point of view, branching should be homogeneous and reproducible, which remains to be solved. The final part of the research addresses this issue and proposes an effective approach for low-temperature synthesis to produce homogeneous TiO_2 mesocrystals and shows the importance of homogeneous branching on the specific surface area (SSA) of rutile mesoparticles, expressed in terms of morphology factor (f_m).

5.1 Homogeneous Mesocrystals

To demonstrate the effect of different synthesis pathways on the final homogeneity of the branches of rutile-type TiO_2 mesocrystals, we resorted to two solution-based synthesis routes, *i.e.* conventional HT method and our new method in laboratory flask. The main difference between the two synthesis approaches is in stirring during mesocrystals

formation. Obtained mesocrystals were further characterized by the SSA measurements which were expressed in terms of f_m . Experimental procedures for the synthesis of 3D mesocrystals and used characterization methods are available under Appendix C.

I. Conventional HT processing. Short-prismatic rutile particles with compact crystals already connected through the 1st twinning relations (for detailed morphological analysis *see* article presented in Chapter 4) were used as seeds in a subsequent HT process under low acidic conditions (0.5 M HCl). This approach results in the formation of 2nd generation twinned branches by the non-classical OA mechanism, whereby short-prismatic nanocrystals self-assemble by low-energy {101} planes of seed crystals and form a secondary twin.

Morphology and phase composition of HT fabricated rutile mesocrystals are shown in Figure 5.1. The branches form randomly on implanted seed rutiles and produce desired spatially branched mesocrystals. A rather non-uniform frequency of branching is due to locally inhomogeneous distribution of titanium source during HT synthesis. From Ti(IV)-butoxide in slightly acidic medium, short-prismatic ECS fibrous rutiles are formed by the two associative condensation processes (*see* article in Chapter 3) that subsequently self-assemble on the seed crystals and form a secondary twin (*see* article in Chapter 4). Due to inhomogeneous conditions across the Teflon-lined autoclave, short rutile nanoprecipitates are not evenly distributed, causing the formation of non-uniform branching. By increasing the supersaturation conditions (Ti(IV)-butoxide concentration), inhomogeneity of branching increases and even leads to the emergence of anatase-phase of TiO₂ due to greater concentration gradients locally present in the batch reactor (*see* article in Chapter 4).

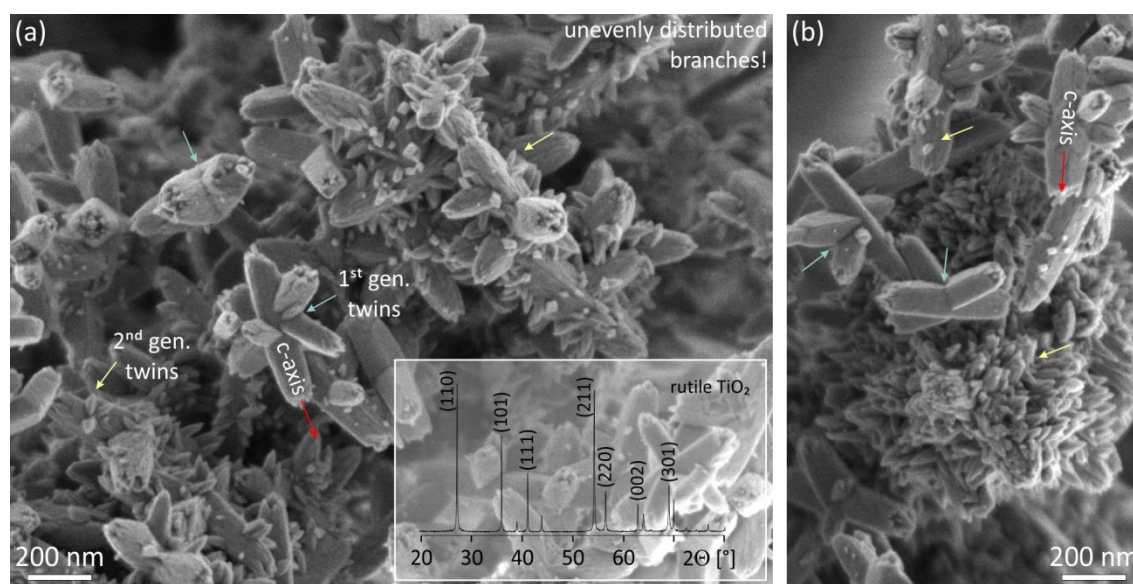


Figure 5.1: Morphology of spatially branched 3D rutile mesocrystals (powder XRD overlay) designed by the subsequent conventional HT synthesis using 12.6 mM Ti(IV)-butoxide. The products stem from different parts of the autoclave, therefore the distribution of newly formed smaller branches (2nd twinning generation, denoted by yellow arrows) on the seed crystals is not homogeneous. Some mesocrystals exhibit more or less branches, depending on the concentration of ECS nano-precipitates each particle is exposed to.

When such inhomogeneous conditions are present during crystals growth, final mesocrystals cannot possess a desired uniform morphology. To design applicable complex self-assembled mesostructures by the OA, inhomogeneity must be avoided.

II. Synthesis in a laboratory flask. Homogeneously branched rutile mesocrystals are prepared by the low-temperature ($\sim 74^\circ\text{C}$) synthesis in a laboratory flask (Figure 5.2). This is achieved by slight stirring of the reactants during the mesocrystal growth. The products exhibit spatially branched rutiles with 2nd generation twins evenly distributed across the entire sample. The frequency of branching proportionally increases with supersaturation conditions, *i.e.* Ti(IV)-butoxide concentration. Regardless of the precursor concentration used mesocrystals morphology, phase composition and density of branching remain uniform, unlike in the conventional HT process. The frequency of twinning can easily be determined. It ranges from ~ 75 (for 12.6 mM, Figure 5.2a), ~ 115 (for 18.9 mM, Figure 5.2b) and to ~ 175 (for 25.1 mM, Figure 5.2c) twins per seed crystal, respectively.

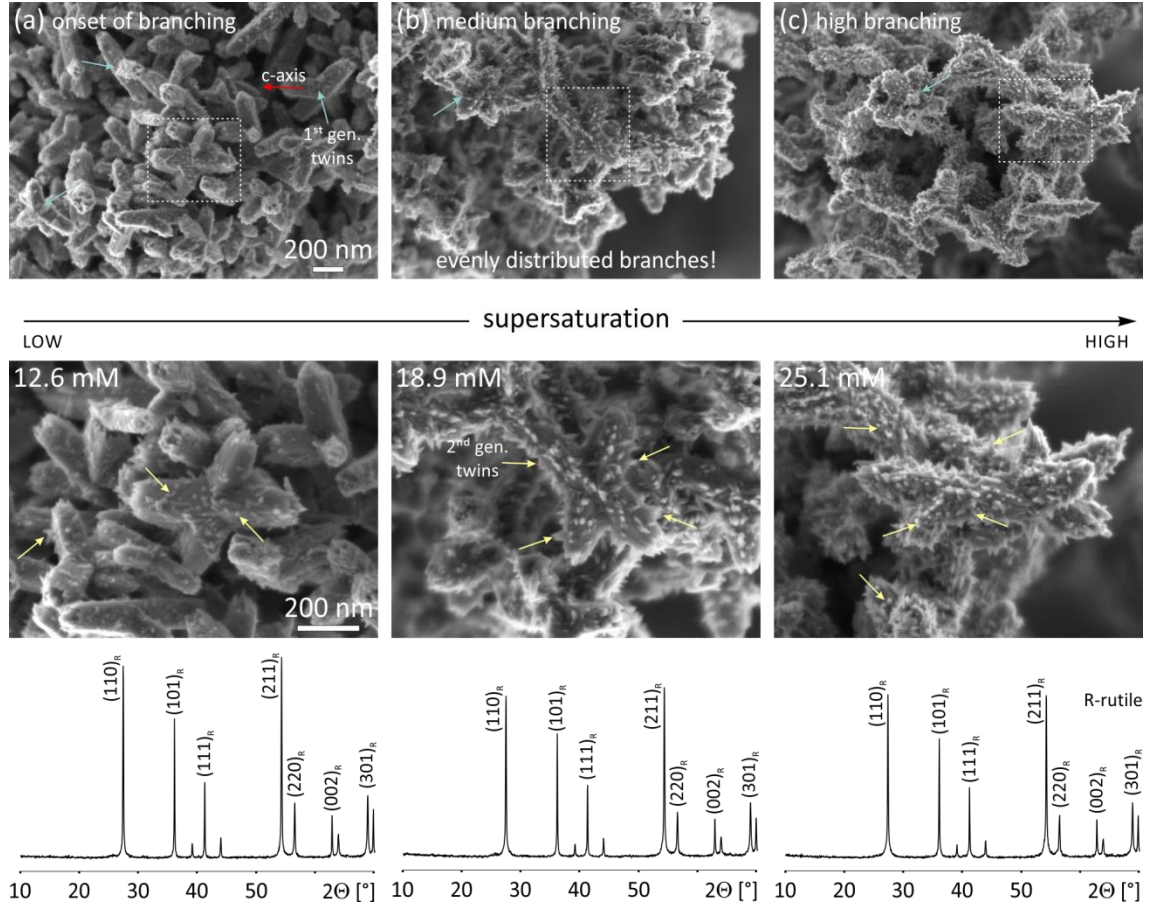


Figure 5.2: Morphology and XRD patterns of homogeneously branched 3D rutile mesocrystals designed by the subsequent synthesis in a laboratory flask, using: (a) 12.6 mM (b) 18.9 mM and (c) 25.1 mM Ti(IV)-butoxide concentration. The products exhibit evenly distributed 2nd generation twinned branches (denoted by yellow arrows) across the entire sample, whereas the density of branching is proportionally increasing with Ti(IV)-butoxide concentration. XRDs correspond to pure rutile-type TiO_2 for all Ti(IV)butoxide concentrations used. Marker in the top left figure corresponds to all the top a-c images, whereas the marker on the bottom left figure to all the bottom a-c images.

With stirring we suppress locally different nucleation conditions and achieve a desired homogeneous precursor distribution, leading to more homogeneous precipitation of rutile nanoprecipitates that subsequently uniformly self-assemble on the implanted seed crystals (*see* article in Chapter 4), resulting in a reproducible monodisperse spatially branched mesocrystals.

III. Morphology factor (f_m). To determine the effect of two synthesis pathways on the SSA, we evaluated f_m of the products. Analysis was done for the samples obtained by our new synthesis approach, which exhibit homogeneously distributed branches across the entire sample (Figure 5.2a-c) and compared to the f_m of morphologically different particles, *i.e.* nonbranched- (rods), seed- (1st twin generation) and meso- (2nd twin generation) crystals with inhomogeneous branching distribution (Figure 5.1), reported in article that is presented in Chapter 4. The corresponding calculations and measurements are listed in Table 5.1.

Table 5.1: Calculated f_m for morphologically different rutile particles, based on the SSAs of the equivalent spherical particles, S_0 calculated from DLS data and actual SSAs of the particles, S measured by BET method. Frequency of 2nd generation twins was determined from the FEG-SEM images.

Branching frequency	D_0 (DLS)	S_0 (DLS)	S (BET)	2 nd gen. twins per seed rutile's	f_m
	[nm]	[m ² /g]	[m ² /g]	[#]	[]
Rutile rods (c-rut)^a	/	/	/	/	1.56
Seed rutile (s-rut)^a	/	/	/	/	2.51
12.6 mM (m-rut): uneven branching ^b	/	/	/	/	5.37
12.6 mM: onset of branching	317.1 ± 5.4	4.47 ± 0.076	41.71 ± 0.432	~75	9.33
18.9 mM: medium branching	471.5 ± 11.8	3.01 ± 0.075	59.42 ± 0.722	~115	19.74
25.1 mM: high branching	638.7 ± 8.7	2.22 ± 0.029	64.44 ± 0.811	~175	29.03

^a products described in article that is presented in Chapter 4.

^b morphologically non-uniform products (Figure 5.1) produced by the conventional HT synthesis, *see* article presented in Chapter 4.

Distribution of twin branches appears to have a significant impact on the SSAs of rutile mesocrystals. In terms of f_m , even distribution of branches on the seed rutiles (Figure 5.2a) produces a 1.7-fold increase of the overall SSA, when compared to mesocrystals prepared by the conventional HT method (Figure 5.1) and further a 3.7- or 5.9-fold increase if compared to the particles with only first- or no-twinning generations (rods), respectively (Table 5.1). This increase is attributed to 2nd generation twinning, its distribution and frequency, as well as the porosity, induced by fibrous growth and lateral OA of nano-precipitates (*see* article in Chapter 4). In addition to the uniformity of branching, its density influences the SSA tremendously (illustrated in Figure 5.3 after FEG-SEM images of the real samples in Figure 5.2a-c). In terms of branching, 1.5-fold increase of precursor concentration (12.6 to 18.9 mM) produces a 2.1-fold increase in f_m , whereas for a 2-fold increase in precursor concentration (12.6 mM to 25.1 mM) the increase is already 3.1-fold. This increase is expected to have a significant impact on the activity of branched mesocrystals for diverse nano-applications.

Low-temperature synthesis strategy in a laboratory flask provides homogeneous distribution of ECS nano-precipitates across the entire batch reactor. This is achieved by constant homogenization (by stirring) of the reactants. The advantage of this synthesis approach is in high reproducibility of the products; regardless of the supersaturation used (Ti(IV)-butoxide concentration) the phase composition and morphology, *i.e.* distribution of secondary branches, remains uniform. This approach does not only induce the desired controlled branching distribution, but also generates a tremendous increase of SSA. Using f_m , we show the significant effects of branching distribution and its frequency on the overall SSA, having a great potential for diverse nanotechnology applications.

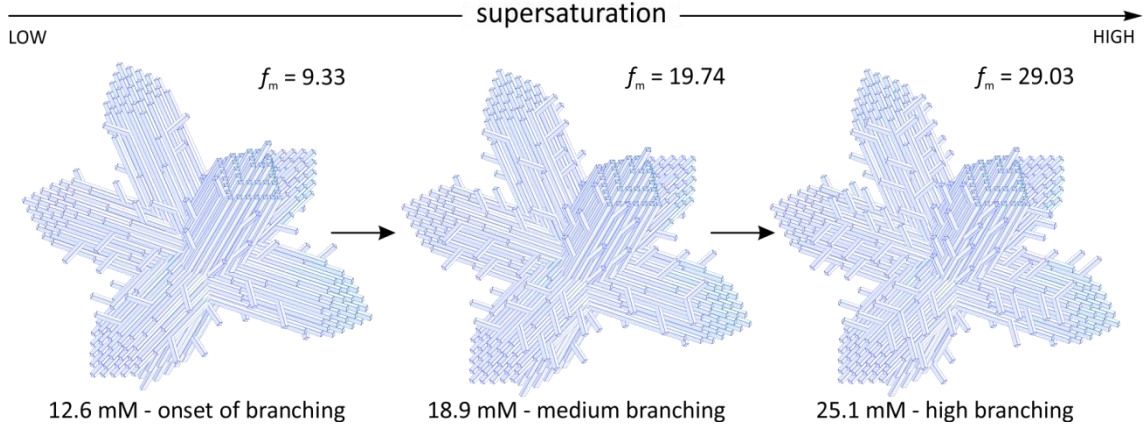


Figure 5.3: Illustration of homogeneous twin-based branching distribution of rutile mesocrystals, proportionally increasing with the supersaturation conditions from 12.6 mM, 18.9 mM and to 25.1 mM Ti(IV)-butoxide concentration (after Figure 5.2a-c).

Chapter 6

Summary and Outlook

6.1 Summary

In this thesis the research was focused on the understanding and ability to control and manipulate crystallization by oriented nanoparticle attachment, whereby first precipitates interact and realign along specific crystallographic directions to achieve a bottom-up design of hierarchical rutile mesocrystals. We succeeded to:

- ∴ identify the growth mechanisms of branched rutile-type TiO_2 mesocrystals,
- ∴ determine the origin and the parameter that controls branching by OA,
- ∴ establish a straightforward scale-up synthesis for the production of reproducible and homogeneously branched mesocrystals for possible applications and
- ∴ introduce a generalized criterion for the characterization of particle's morphology.

Rutile-type TiO_2 mesocrystals were synthesized using the HT synthesis method. The foremost effort was dedicated to resolving the mechanism controlling its formation. During the first step of research it was confirmed that the growth of rutile mesocrystals is driven by the self-assembly mechanism, where branching is a result of twinning. Here, twinning was recognized as a self-assembly process that can be tailored to produce multilevel branched architectures. The key processes of rutile mesocrystals growth can be divided into two main steps. First, nucleation of rutile fibers *via* hydrolysis and condensation reactions takes place. We identified that hydrolysis happens at room temperature and that the acidity not only defines the type of complexes in the reactive solution but also dictates the rate of their condensation through repulsive electrostatic forces. Additionally it determines the balance between ololation (defines the length of 2D octahedral chains) and oxolation (combines the linear chains into 3D crystal structures) reactions and thus defines the ECS of the first precipitates. In the next step, ECS rutile precipitates undergo self-assembly in two ways: (i) along low-energy $\{110\}$ crystal planes – lateral growth and (ii) along low-energy $\{101\}$ crystal planes – twinning. The process of self-assembly is composed first of ECS precipitates alignment by the shape-specific electromagnetic vdW interactions (~ 20 nm), followed by their crystallographic alignment by the structure-specific interactions (< 5 nm), and finally concluded by hydrogen bonding and dehydration processes (< 1 nm) that lock the nanoparticles into a mesocrystal structure. The presence of theoretically estimated force-fields conveying important structural information through which OA is even possible was identified by the HRTEM. These results are an unambiguous proof that surface energy reduction is not the main driving force for the self-assembled growth of rutile mesocrystals.

Our study revealed that acidity controls twinning by OA through ECS of precipitates. This was further confirmed by using seed rutile crystals as templates for continued homo-epitaxial growth and growth by the OA of nanocrystals along low-energy

planes. We showed the dependence of self-assembly on the nanocrystals aspect ratio, where the possibility of twin incidents is highly increasing with the decrease of the nanoparticles length. This is due to the fact that the surface areas of the two assembling planes, *i.e.* $\{110\}$ and $\{101\}$ become more comparable and thus in addition to lateral assembly, twin assembly becomes possible. A threshold point for ECS precipitates that still assemble in twin orientation was set to $l/w \sim 3$. By utilizing the aspect ratio of precipitated nanocrystals, the desired mesocrystals morphology can thus be obtained. Gained knowledge on how to induce twin-incidents by the self-assembly of rutile nanocrystals was further used to design applicable branched rutile mesocrystals. Contrary to the conventional HT method, constant homogenization during mesocrystals growth was applied, which led to reproducible samples with homogeneous branching, regardless of the supersaturation conditions. This low-temperature synthesis approach is now opening new prospects for industrial scale-up and opportunity to test the samples in preferred applications.

Finally, to evaluate the effect of branching and its overall contribution to the specific surface area, we established a universal criterion, *i.e.* morphology factor (f_m). This criterion was developed, since at present the nano-research community has no quantitative tool to compare and evaluate a variety of prepared morphologies, regardless of the sample sizes. Using f_m the increase of specific surface area with twin generations, their distribution density and homogeneity was shown.

6.2 Outlook

The described mechanisms and the first experimental proof of force-fields (Jordan *et al.* (2016) [214] *Scientific Reports*) present during mesocrystals growth have a potential to open the possibilities of exploiting electrostatic forces along with fully grown nanocrystal building units, and boost a bottom-up engineering of multifunctional sensors and catalysts that require high specific surface areas approaching that of fractals. Moreover, the new criterion for the evaluation of nanoparticle morphology and branching (Jordan *et al.* (2018) [216] *Crystal Growth and Design*) is simple to implement, applicable to any kind of nanomaterials, and will be highly appreciated by the nano-research community that has no quantitative tool to compare diverse morphologies.

Although several ground breaking tasks were resolved within this thesis, still a lot of new challenges arise which are waiting to be answered. One of the unresolved issues that remain are the condensation reaction pathways between titanium complexes in the aqueous reaction medium. In this thesis, formed titanium complexes and their possible condensation paths were discussed and suggested, however the experimental and/or theoretical proof still needs to be provided. Next, recent studies revealed that self-assembly is a complex mechanism and most probably a sum of various driving forces between the identified building units. Within this thesis, building units of rutile's mesocrystal growth were identified and surface energy reduction was excluded as a possible driving force for their OA. Additionally, rutile has no permanent dipole and therefore dipole-dipole interactions can also be excluded. On the contrary, charge fluctuating vdW interactions have recently become recognized as possible driving forces of self-assembly for rutile. These forces are typical for anisotropic and birefringent materials such as rutile, but are also influenced by the solvent's properties and associating ligands, presence of unsatisfied crystal's surface bonds (materials intrinsic properties), its propensity to dissociate water molecules, *etc.*, that need to be taken into account. Identification of the true nature of attractive forces for oriented assembly between the identified rutile building blocks, leading to final hierarchically branched

rutile crystals, is an exciting new challenge, which needs further theoretical and *in-situ* experimental studies. The *in-situ* techniques are especially important since they allow direct observation of the mesocrystals formation, which will improve our understanding of their growth mechanisms based on spontaneous interactions between the building units. Further goal would therefore be to design molecular-scale experiments targeted to identify principal forces that drive orientation-specific particle alignment and assembly, and build corresponding theory that will entangle experimentally confirmed mechanisms, and provide protocols for tailoring mesocrystalline structures *via* self-assembly. Finally, prepared homogeneously branched mesocrystals need to be tested in possible applications. Appropriate applications are the ones where high specific surface areas are needed, such as separation technologies, where the use of branched mesocrystals can resolve the current dilemma of having either a large surface area necessary for high capacity, or large pores required for high permeability, but not both.

Appendix A

Self-Assembly of Multilevel Branched Rutile-Type TiO₂ Structures Via Oriented Lateral and Twin Attachment

Data presented in this Chapter supplement the article introduced in Chapter 3.

A.1 Article's Supporting Information

The following materials provide additional information on the influence of HT synthesis parameters on the morphology and phase composition of the products, calculations for OH⁻/H⁺ ratio and partial charges (δ) of ligands for polycondensates produced by the olation process.

∴ Calculation of OH⁻/H⁺ ratio

By increasing the acidity of the reactant medium, OH⁻/H⁺ ratio is decreased, *i.e.* c[OH⁻] is reduced. For the calculation of OH⁻/H⁺ ratio we can use two equations [87]:

$$K_{\text{H}_2\text{O}} = c[\text{H}_3\text{O}^+] \cdot c[\text{OH}^-] = 10^{-14} \quad (\text{S1})$$

$$c[\text{OH}^-] = K_{\text{H}_2\text{O}}/c[\text{H}^+] \quad (\text{S2})$$

where $K_{\text{H}_2\text{O}}$ is the dissociation constant of water and $c[\text{H}^+]$ is the molar concentration of the acid. Reduction of the $c[\text{OH}^-]$ and OH⁻/H⁺ ratio when using hydrochloric acid is summarized in Table S1.

Table S1: Calculated values for $c[\text{OH}^-]$ and OH⁻/H⁺ ratio for pure water and hydrochloric acid of different molarities, showing their decrease as a function of acid concentration.

	$c[\text{OH}^-]$ [M]	OH ⁻ /H ⁺ ratio []
H ₂ O	10 ⁻⁷	1
4.4 M HCl	2.27·10 ⁻¹⁵	5.16·10 ⁻¹⁶
5.5 M HCl	1.82·10 ⁻¹⁵	3.31·10 ⁻¹⁶

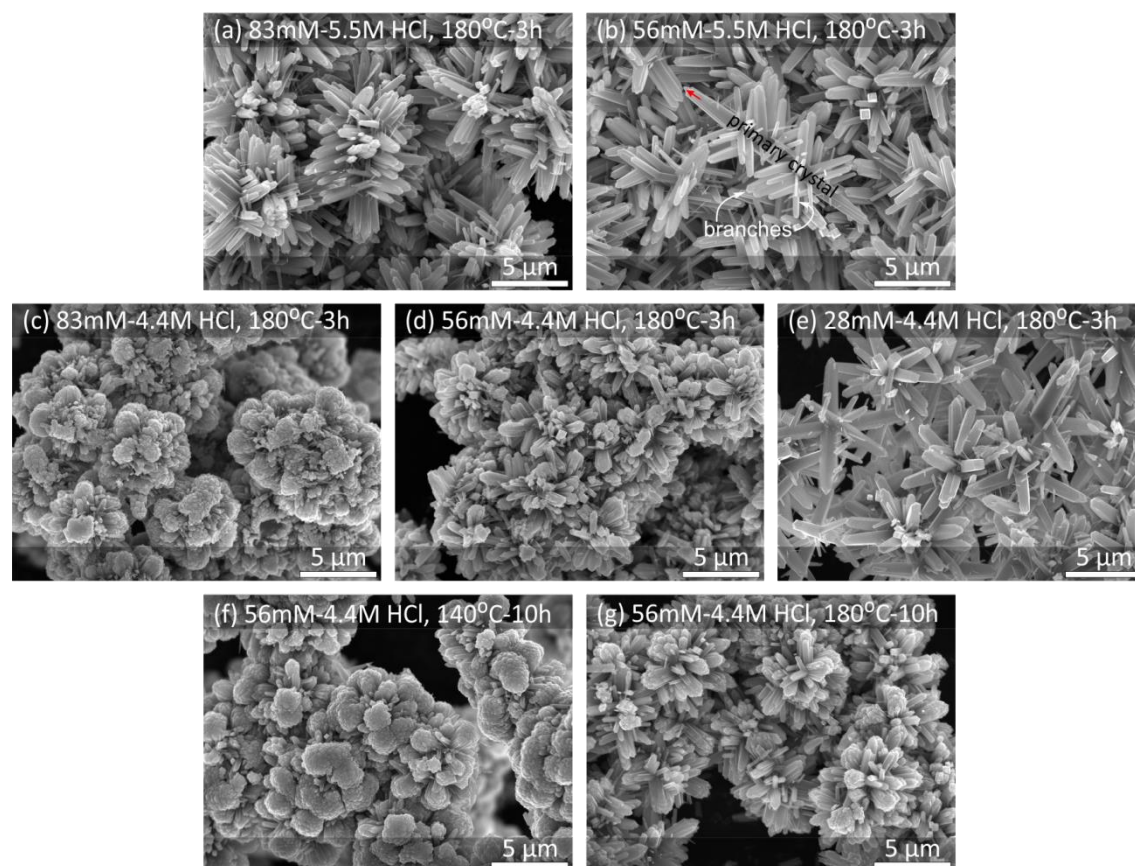


Figure S1: Reactive HT processing of titanium(IV) butoxide showing different modes of branching under varied synthesis conditions. HT synthesis using 5.5 M HCl (low reactant conditions, *i.e.* low OH⁻/H⁺ ratio) with titanium(IV) butoxide precursor concentrations of (a) 83 mM and (b) 56 mM and target temperature of 180 °C for 3 h, yields longer rutile crystals which are displaying similar angular contacts as those obtained at higher reactant and lower precursor concentrations, *i.e.* (d) and (e). The main difference between (a) and (b) is noticeable by the thickness of primary crystals; at higher precursor concentration (83 mM) primary crystals are thicker when compared to the primary crystals obtained at a lower precursor concentration (56 mM). Images (c) – (e) show products obtained at higher reactant concentrations (4.4 M HCl) as a function of decreasing precursor concentration at a constant temperature and time (180 °C and 3 h). (c) With higher precursor concentration, spherulitic particles consisted of numerous ultrafine rutile fibers radiating from the common center are formed. (d) With decreasing the concentration of the precursor, rutile particles are less dense and show fewer and more visible branches where numerous possible twin incidences and other types of intergrowths can be identified. (e) On further decrease of the precursor concentration, well defined multilevel branched crystals of rutile are produced. (f) At lower temperature (140 °C) the products become spherulitic, indicating a higher degree of supersaturation than that at a higher temperature, *i.e.* nuclei are smaller and consequently their concentration is higher [77]. (g) The increase of synthesis time (10 h) shows no significant influence on the final product's morphology, compared with products in (d) and (g). In summary, for the production of highly branched rutile-type TiO₂ (based on twinning) we need the following HT conditions: (i) high temperature, (ii) low precursor or (iii) low reagent concentration.

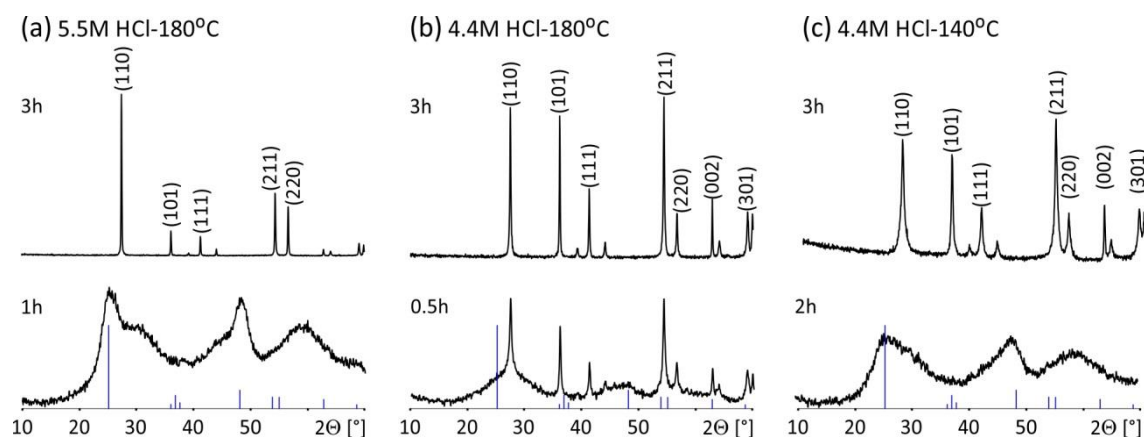


Figure S2: XRD patterns of HT synthesized rutile: (a) in 5.5 M HCl at a target temperature of 180 °C for 1 and 3 h, (b) in 4.4 M HCl at a target temperature of 180 °C for 0.5 and 3 h, and (c) in 4.4 M HCl at a target temperature of 140 °C for 2 and 3 h. Titanium(IV) butoxide concentration was held at 56 mM. For all compositions sharp reflections correspond to the rutile-type TiO_2 . After shorter processing times (below) these compositions show the presence of amorphous material, suggesting anatase-type TiO_2 ordering (blue).

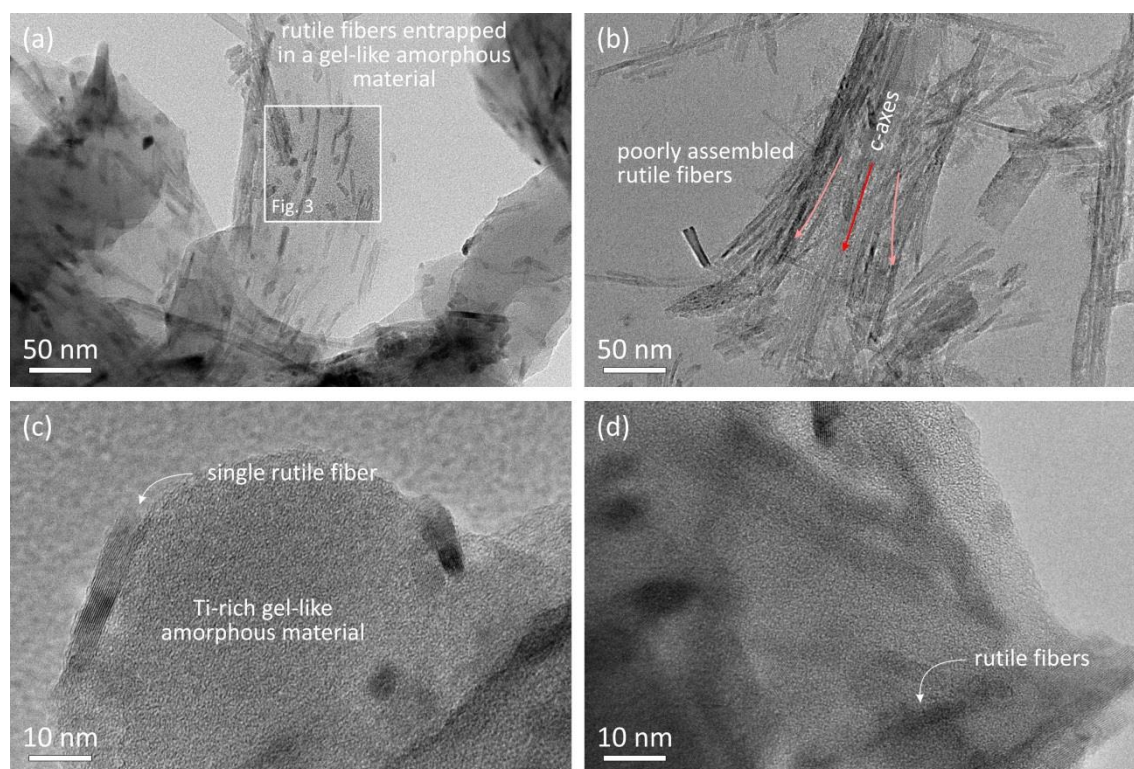


Figure S3: Nucleation of fibrous rutile from a titanium rich amorphous precursor. (a) Gel-like material present after a short time of HT treatment contains isolated equilibrium shape rutile fibers that formed by condensation reactions (*see* article, Figure 7). Precipitated fibers are generally disordered, however in some parts they appear to be aligned in parallel, regardless of the considerable distance (~ 20 nm) between them (for details on short-range self-assembly *see* article, Figure 4). (b) Onset of fiber assembly. Several rutile fibers in a cluster show a general alignment along the crystallographic *c*-axis. (c, d) Details of amorphous titanium-precursor with isolated rutile fibers, produced

through oxolation reaction. Darker sections correspond to vertically aligned rutile fibers embedded in a gel-like material.

Table S2: Calculations of partial charge increase in various titanium complexes formed by protonation and ololation reaction: Calculated partial charges of titanium complexes formed by the ololation reaction between different initially protonated complexes (depending on the medium acidity), using a model proposed by Livage *et al.* (1988) [197]. With ololation reaction and formation of positively charged complexes due to protonation, partial charges of OH ligands are increasing, therefore losing their nucleophilic power. If initially complexes are not protonated (0 complexes) or slightly protonated (1⁺ complexes), ololation can start easily and continue until OH ligands on titanium cation remain negatively charged. However, if initially complexes are highly charged, ololation reaction is stopped when a dimer is formed in the case of 2⁺ complexes or not possible for 3⁺ complexes.

Complexes by ololation	$\delta(\text{Ti})$	$\delta(\text{O})$	$\delta(\text{H})$	$\delta(\text{OH})$	$\delta(\text{H}_2\text{O})$
[Ti(OH) ₄ (OH ₂) ₂] ⁰	0.753	-0.394	0.2014	-0.193	0.0088
[Ti ₂ (OH) ₈ (OH ₂) ₂] ⁰	0.755	-0.393	0.202	-0.191	0.011
[Ti ₁₀ (OH) ₄₀ (OH ₂) ₂₀] ⁰	0.753	-0.394	0.201	-0.193	0.008
[Ti(OH) ₃ (OH ₂) ₃] ¹⁺	0.821	-0.353	0.255	-0.098	0.157
[Ti ₂ (OH) ₆ (OH ₂) ₄] ²⁺	0.837	-0.343	0.268	-0.075	0.193
[Ti ₁₀ (OH) ₃₀ (OH ₂) ₁₂] ¹⁰⁺	0.857	-0.331	0.284	-0.047	0.237
[Ti ₂₀ (OH) ₆₀ (OH ₂) ₂₂] ²⁰⁺	0.86	-0.329	0.286	-0.043	0.243
[Ti ₄₀ (OH) ₁₂₀ (OH ₂) ₄₂] ⁴⁰⁺	0.861	-0.328	0.287	-0.041	0.246
[Ti ₄₅₀ (OH) ₁₃₅₀ (OH ₂) ₄₅₂] ⁴⁵⁰⁺	0.863	-0.327	0.289	-0.038	0.251
[Ti(OH) ₂ (OH ₂) ₄] ²⁺	0.88	-0.316	0.302	-0.014	0.288
[Ti ₂ (OH) ₄ (OH ₂) ₆] ⁴⁺	0.908	-0.299	0.324	0.025	0.349
[Ti(OH)(OH ₂) ₅] ³⁺	0.932	-0.285	0.343	0.058	0.401
[Ti ₂ (OH) ₂ (OH ₂) ₈] ⁶⁺	0.968	-0.263	0.371	0.108	0.479

Appendix B

Material's Design Beyond Lateral Attachment: Twin-Controlled Spatial Branching of Rutile TiO₂

Data presented in this Chapter supplement the article introduced in Chapter 4.

B.1 Article's Supporting Information

The following materials provide additional information on performed calculations and conducted measurements, including details on phase composition and morphology of the samples.

∴ Calculations of the effective surface and porosity as a function of branching for hypothetical multiple twinning of rutile TiO₂ (article, Figure 1b)

To predict the effect of branching on the effective surface area and porosity, a simple geometrical model of fractal twinned rutile was considered, as illustrated in article's Figure 1b. In this model a tetragonal prismatic morphology of individual crystals was assumed with l/w ratio of 8. For simplicity, crystal terminations were flat without any pyramid faces. The length of the primary rutile crystal was 5 μm , with subsequent twin generations set to 20 % of the previous size. Each new generation follows $\{101\}$ twin law on each prism face of the parent rutile crystal [152]. Twinning on grandparent crystals is excluded. Following this rule, the total number of crystals N follows a geometric series:

$$N = 1 + \sum_{i=1}^n 4^i \quad (\text{S1})$$

The effective surface was calculated by summing the surface area of all crystals in the new generation, i , and added to the previous total, decreased by the attachment surface according to the twin rule. For porosity, rectangular cell occupied by fully evolved fractal cluster with infinite twin generations was used (~ 20 generations were sufficient for estimation), and then the void volume was calculated by subtracting branched rutile's volume from cell's volume for each generation.

∴ Characterization of the reference sample (c-rut)

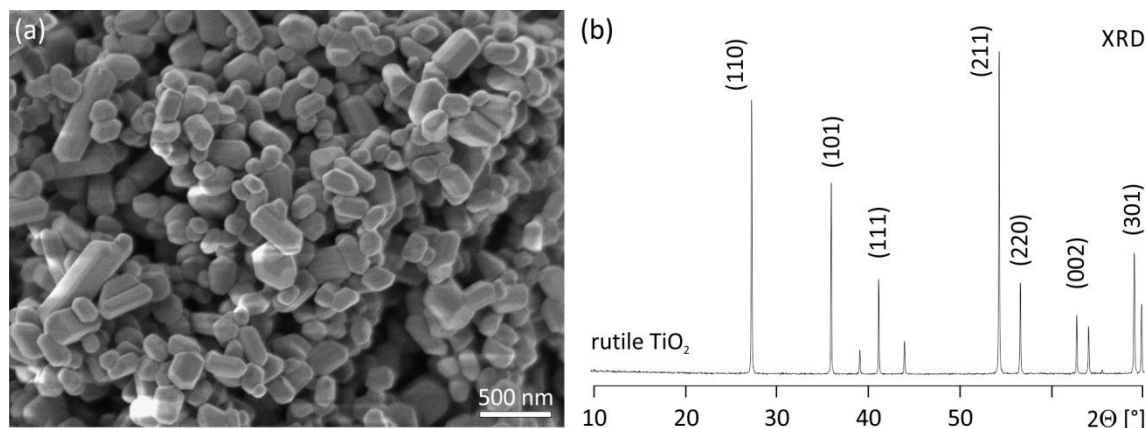


Figure S1: Commercially available reference rutile sample (c-rut) from Cinkarna Celje, Slovenia. (a) FEG-SEM image showing short-prismatic nanocrystals and corresponding (b) powder XRD pattern confirming that the product is a rutile phase of TiO₂. The lengths of the crystallites range from 140 – 450 nm and are 70 – 140 nm wide with an average l/w aspect ratio of ~ 2.8 .

∴ Aspect ratio of precipitated rutile fibers (m-rut)

The aspect ratio of precipitated rutile fibers depends on the acidity of the reactive medium.

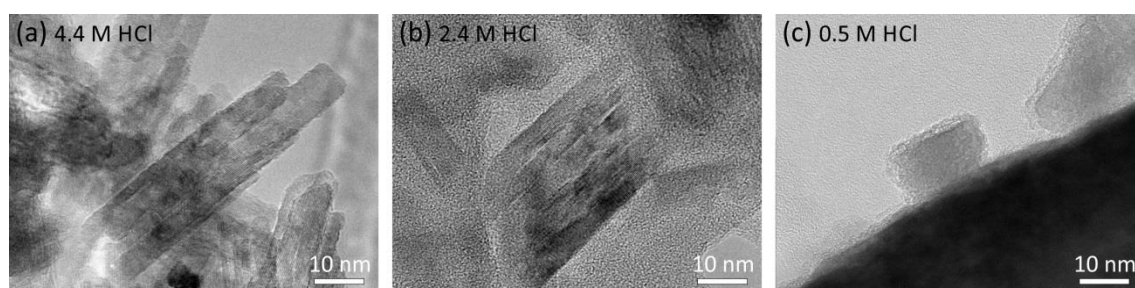


Figure S2: Representative TEM images of precipitated rutile fibers under changing acidic conditions: (a) 4.4 M HCl, (b) 2.4 M HCl and (c) 0.5 M HCl. Several fibers were measured and corresponding l/w aspect ratios; 12, 7, and 2.7 have been obtained, respectively. Linear dependence of l/w vs. medium acidity is shown in article's Figure 5. Conditions under (a) and (b) show lateral OA whereas in (c) twin OA becomes more abundant.

∴ High precursor concentration leading to the formation of anatase phase (m-rut)

The presence of anatase phase is to be expected whenever the repulsion forces between the titanium complexes drop below the rutile stability range, where anatase nucleation is favored, and are critical for low acidity, low temperature and high precursor concentration conditions [214]. Minor anatase can also form due to local supersaturation conditions in the initial stages of precipitation.

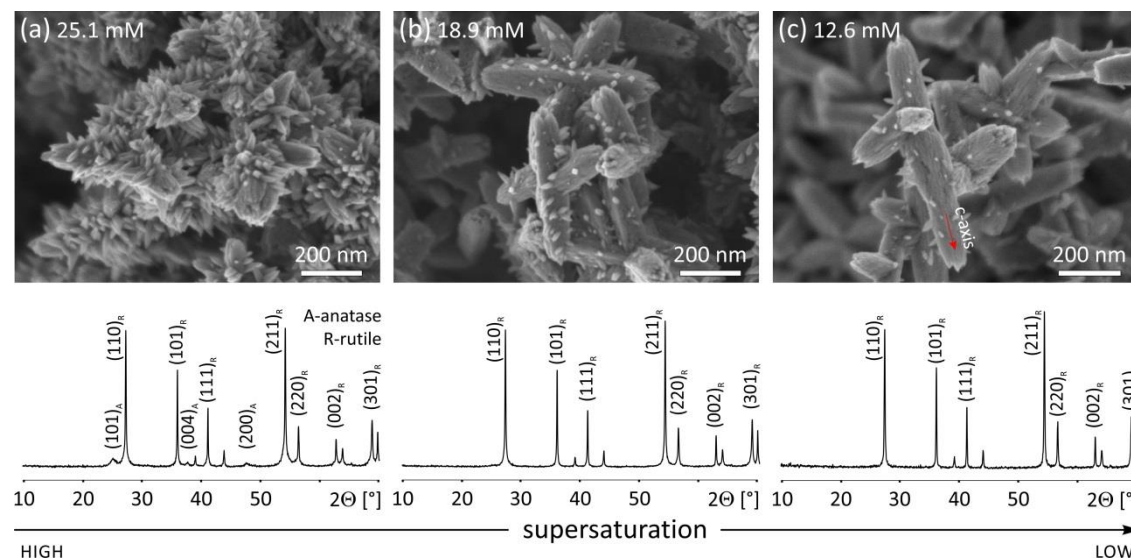


Figure S3: XRDs of branched m-rut, shown in article's Figure 6: (a)-(c) XRDs confirm the good crystallinity of rutile-type TiO_2 , accompanied by a small amount of anatase phase of TiO_2 at higher supersaturation conditions, seen in (a). m-rut were synthesized in 0.5 M HCl at 100 °C for 2 h using different titanium(IV) butoxide concentrations.

∴ The effects of local inhomogeneities in growth conditions (m-rut)

During HT synthesis in batch reactors the morphology of the products can vary significantly. One of the main problems is heterogeneous nucleation on the Teflon-lined reactor walls, where product morphology evolves differently than homogeneously nucleated crystals that freely precipitate from the solution. This effect is partly avoided by using seed crystals as in our study. In this way we have a heterogeneous nucleation within the entire volume of the reactor and the morphology is more uniform. Deviations can be best seen in different aspect ratio of precipitates and frequency of branching.

However, the number of branches does not differ only because of locally different nucleation conditions, but can be reduced due to detachment, as previously observed by other authors [115].

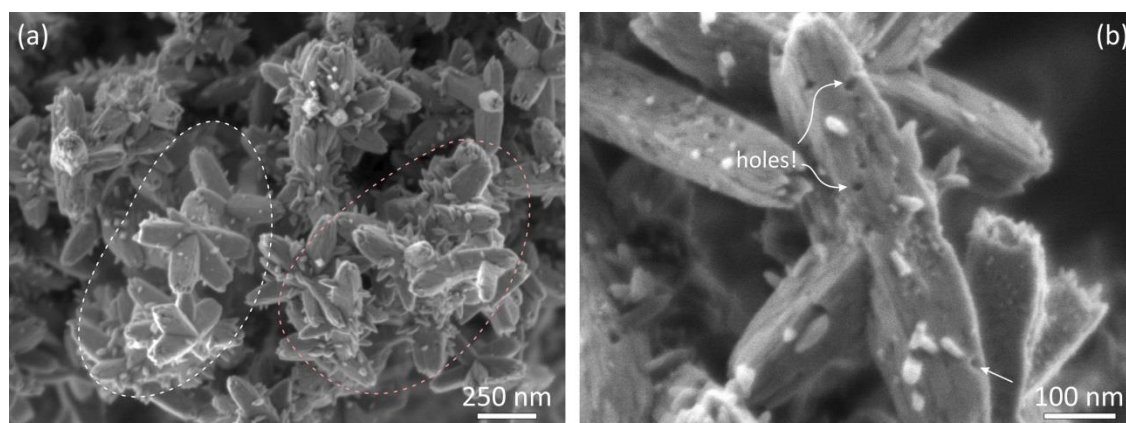


Figure S4: Larger differences in growth conditions are imminent when using HT batch reactors with larger volumes, preventing a simple scale-up: (a) product of 4-fold increased batch synthesis of m-rut with 12.6 mM titanium(IV) butoxide HT treated in 0.5 M HCl for 4 h, 100 °C (compare with article's Figure 6a) showing a rather nonuniform frequency of branching – regions of higher frequency are outlined red, opposed to scarce branching,

outlined white. The products stem from different parts in the autoclave. The aspect ratio of precipitates is consistent for these growth conditions. (b) Some m-rut crystals show detachment of branches (holes).

∴ Sphericity and specific surface area of non-spherical particles

Numerous nanotechnology applications require materials with a large effective surface area, and diverse branched materials are being produced to satisfy the emerging technological demands. To quantify particle branching, we introduce a morphology factor, f_m that defines a relative increase of an effective surface area of a particle compared to that of a sphere with the same volume. Among all geometric shapes a sphere has the smallest surface area per volume it occupies. Any deviation from the spherical shape is defined by a sphericity of the particle, Ψ , a ratio between the surface area of a sphere and that of a particle with the same volume [215]:

$$\Psi = \frac{A_0}{A} = \frac{\pi^{1/3}(6V)^{2/3}}{A} \quad (S2)$$

where V is the particle volume, A is its surface area, and A_0 is the surface of a sphere. For the spherical particle, where $V = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$ sphericity, $\Psi = 1$, whereas for any other particle $\Psi < 1$. Our morphology factor, f_m , is defined as the increase of a specific surface area and is thus reciprocal of Ψ :

$$f_m = \frac{S}{S_0} = \Psi^{-1} [] \quad (S3)$$

where S is a specific surface area (SSA) of the particle, and S_0 is SSA of an equivalent sphere:

$$S_0 = \frac{A_0}{V_0 \cdot \rho} = \frac{3}{r \cdot \rho} [m^2/g] \quad (S4)$$

in terms of the effective hydrodynamic diameter ($r = \frac{1}{2} D_0$) equation S4 can be rewritten as equation 2 (main article's text). Table S1 lists f_m 's for some characteristic shapes for comparison with Table 1 in the article.

Table S1: Calculated morphological factors for simple geometric forms, where it is assumed that the volume of a particle is identical to the volume of sphere ($V=V_0$).

Form *	V	A	f_m
Octahedron	$\frac{\sqrt{2}}{3} \cdot a^3$	$2\sqrt{3} \cdot a^2$	$\frac{2\sqrt{3} \cdot a^2}{4\pi \cdot r^2} = \sqrt[3]{\frac{6\sqrt{3}}{\pi}} = 1.18$
Cube	a^3	$6 \cdot a^2$	$\frac{6 \cdot a^2}{4\pi \cdot r^2} = \sqrt[3]{\frac{6}{\pi}} = 1.24$
Tetrahedron	$\frac{\sqrt{2}}{12} \cdot a^3$	$\sqrt{3} \cdot a^2$	$\frac{\sqrt{3} \cdot a^2}{4\pi \cdot r^2} = \sqrt[3]{\frac{3\sqrt{3}}{\pi}} = 1.49$

* expressed in terms of polyhedral edge, a , and radius of equivalent sphere, r .

∴ DLS measurements of effective hydrodynamic diameters of rutile particles, D_0

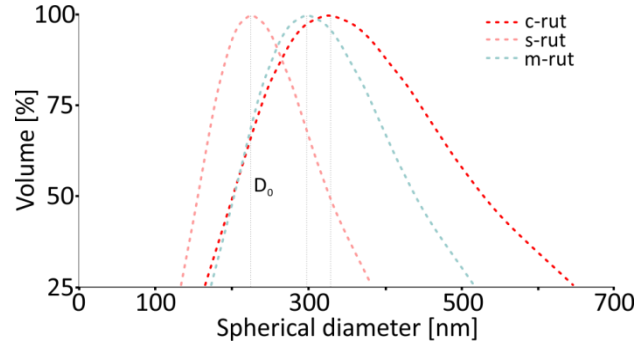


Figure S5: DLS measurement. 0.04 g/l of particles were dispersed in Mili-Q water in an ultrasound bath and an ultrasonic processor. The samples exhibit a characteristic lognormal particle size distribution: c-rut has the broadest particle size distribution with the average D_0 of 326.0 nm, this is followed by branched m-rut with D_0 of 298.4 nm, and s-rut with D_0 of 225.4 nm.

∴ Dimensions of particles, calculated specific surface areas and morphology factors

In order to estimate the effective surface areas and volumes of the samples independently of DLS and BET measurements, dimensions of rutile particles (c-, s- and m-rut) were measured from FEG-SEM images. Average surface area, A' , and volume, V' , of particles were calculated based on measuring the length (l ; along c-axis) and the width (w ; width of {110} prisms) of individual crystals. From the rutile a-, and c-axes ($a = 4.5922$ nm, $c = 2.9578$ nm) [221], the height of the pyramids in prismatic {110} crystals terminated by {111} planes is $\sim 0.46 \cdot w$ that was used in calculations. In the reference c-rut sample the crystals were assumed to be loose, whereas in the s-rut and m-rut clusters crystals are connected through twinning. We estimate ~ 6 twins (1st gen.) in an average s-rut cluster, whereas in m-rut samples we have ~ 25 twins (2nd gen.) per parent branch on average. Dimensions of parent m-rut clusters were measured as they were compact, with the porosity due to fibrous growth not taken into account. Any increase in length and width of the base crystals, due to growth and lateral OA, was attributed to the dimensions of parent s-rut. The measurements are listed in Table S2.

Table S2: Average dimensions of c-rut, s-rut and m-rut crystals based on measurements from FEG-SEM and TEM images. Each generation is measured separately and multiplied by the number of branches (6 in the 1st generation of twins and 25 per branch in the 2nd). Volume, V' , and surface area, A' , are calculated for individual crystals in c-rut sample and twinned clusters for s-rut and m-rut.

particle	parent crystal $l \times w$ [nm]	1 st gen. twin $l \times w$ [nm]	2 nd gen. twin $l \times w$ [nm]	V' [nm ³]	A' [nm ²]
c-rut	140÷450 × 70÷140	n.a.	n.a.	$2.543 \cdot 10^6$	$135.4 \cdot 10^3$
s-rut	n.a.	120÷230 × 50÷90	n.a.	$3.569 \cdot 10^6$	$255.3 \cdot 10^3$
* m-rut	n.a.	190÷310 × 60÷110	20÷40 × 7÷15	$8.408 \cdot 10^6$	$627.0 \cdot 10^3$

* 12.6 mM titanium(IV) butoxide HT treated in 0.5 M HCl for 4 h, 100 °C, scale-up.

From V' the effective sphere diameter, D_0' , and surface area, A_0' , were calculated. Hence, sphericity of the particles was calculated using equation S2. Alternatively, the corresponding morphology factors for particles were calculated using equation S3. In SSA calculations, rutile density of 4.23 g/cm³ was used.

Table S3: Calculated diameters, D_0' , and surface areas, A_0' , for spherical particles with an equivalent volume, V' . SSA's of particles, S' , and equivalent spheres, S_0' , were calculated using equation S4.

particle	eff. sphere D_0' [nm]	eff. sphere A_0' [nm ²]	sphericity Ψ' []	SSA sphere S_0' [m ² /g]	SSA particle S' [m ² /g]	morphology f_m' []
c-rut	169.4	$90.1 \cdot 10^3$	0.666	8.38	12.58	1.502
s-rut	189.6	$113.0 \cdot 10^3$	0.442	7.48	16.91	2.260
* m-rut	252.3	$199.9 \cdot 10^3$	0.319	5.62	17.63	3.140

f_m' is used only for comparison with measured f_m and is not a reliable measure of branching.

∴ Twin assembly of precipitated particles

Precipitates, as soon as they are formed, seek to assemble with other particles in low energy configurations. Along with {110} lateral assembly rutile is also assembled in twin orientations.

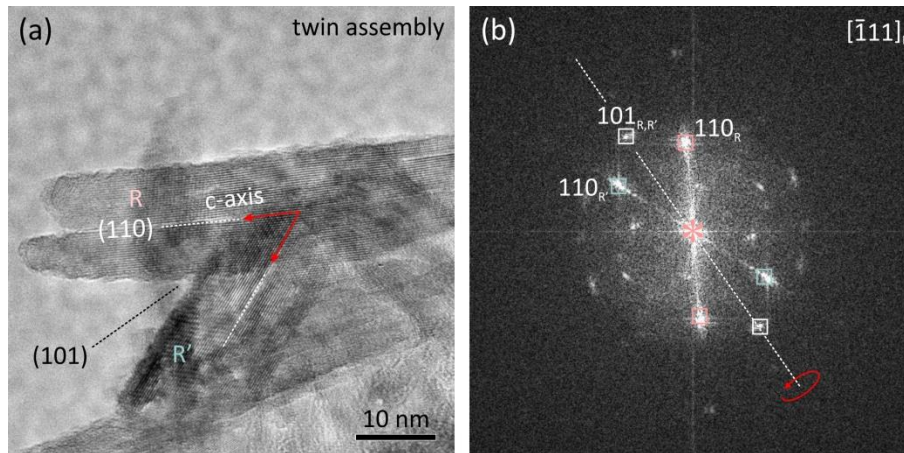


Figure S6: Self-assembly of precipitated rutile fibers. (a) TEM image shows prismatic rutile crystals assembled in (110) lateral as well as in (101) twin orientation, as shown by (b) FFT of the cluster in which the two crystals are related to each other by 180° rotation around the [101] twin axis.

∴ Precipitation of anatase and its attachment to rutile surfaces

Under high supersaturation conditions when dehydration processes are fast (Figure S3a), anatase can precipitate along with rutile. It tends to form assembled clusters on its low-energy (101) planes, or they are attached to rutile (110) planes. As there is no close structural relation between the two polymorphs their crystallographic relation is incoherent.

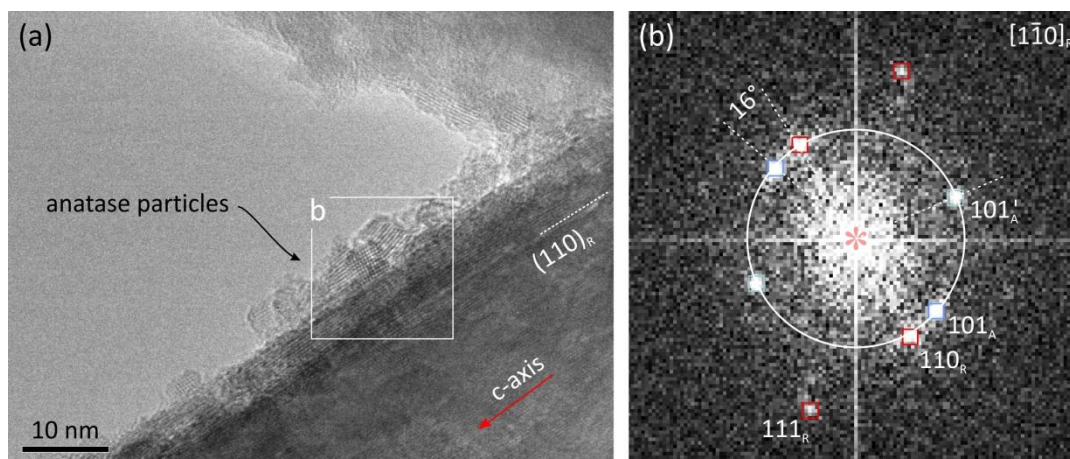


Figure S7: Attachment of anatase TiO_2 particles onto rutile surfaces. (a) TEM image showing a few nanometers large anatase particles perched on the (110) rutile surface. (b) FFT of the area marked in (a) with strong {110} rutile (red) and {101} anatase (blue-green) reflections. Anatase is not in any orientation relation with the parent rutile. Upper crystal (blue) has 16° mismatch with the corresponding rutile plane, whereas the lower (green) is almost perpendicular to the rutile surface. Note the slightly smaller d-spacing of (110)_R vs. (101)_A.

Appendix C

Low-Temperature Synthesis of Hierarchical Rutile-Type TiO₂ Mesocrystals

Data presented in this Chapter supplement the results discussed in Chapter 5.

C.1 Experimental and Characterization Methods

∴ Synthesis of 3D mesocrystals.

In the first step, compact TiO₂ crystals used as rutile seeds in the subsequent mesocrystals growth were prepared as described in article presented in Chapter 4. Appropriate amount of seed crystals was used for the production of final 3D branched mesocrystalline rutile, using two synthesis procedures, *i.e.* conventional HT growth and our new synthesis approach based on stirring of the reactive solution during mesocrystals growth. With this we were able to establish the effects of stirring on the branching distribution of mesocrystalline rutile, produced through crystal twinning by OA.

In both syntheses, 44.4 mg of seed crystals were dispersed in 39.9 ml of 0.5 M hydrochloric acid (HCl; 37% Carlo Erba) directly in 102 ml Teflon cups or a 100 ml laboratory flask, respectively. Dispersion of particles was achieved by an ultrasonic bath (model Sonis 4, Iskra PIO d.o.o., Šentjernej, Slovenia) for 8 min and additional mixing at 400 rpm for another 15 min. After homogenization, titanium butoxide (Ti(IV)-butoxide; 97% Sigma-Aldrich) was added dropwise into suspension to achieve concentrations of 12.6 - 25.1 mM and additionally mixed for 15 min. Conventional HT synthesis was carried out by the use of stainless steel autoclaves where the reactive solution was exposed to 100 °C for 4 h, whereas in our new approach, laboratory flask closed with an appropriate stopper was put on a stirrer heated to 100 °C and mixed at 300 rpm for 4 h. After the synthesis in a laboratory flask, the temperature in the solution was immediately measured and it ranged from 71 - 76 °C. White precipitate from the solution in both approaches was collected, centrifuged, washed in absolute ethanol 4-times and dried in air at room temperature. The final mass of obtained TiO₂ mesocrystals was ~ 70 - 100 mg, depending on the Ti(IV)-butoxide concentration used.

∴ Characterization methods.

Phase composition, morphological characteristics, distribution and frequency of secondary branches on synthesized mesocrystals were characterized by powder X-ray diffractometry (XRD; model PANalytical X'Pert High-Resolution PRO, Almelo, the Netherlands) from

10° to 80° and by field-emission scanning electron microscope (FEG-SEM; model JSM-7600F, Jeol Ltd., Tokyo, Japan), respectively.

For effective quantification of branching, morphology factor (f_m) was determined based on dynamic light scattering (DLS) technique and specific surface areas (SSA) measurements. With DLS, (PALS, ZetaPALS Potential Analyzer, Brookhaven Instruments Ltd., New York, USA, beam wavelength of 658 nm, a run time of 3.3 min and a scattering angle of 90°) effective (hydrodynamic) diameter (D_0) of a spherical particle that diffuses similarly as investigated particles and their corresponding polydispersity indexes (PDI) were measured. The collected data was analyzed for the set of experimental parameters (BIC Particle Sizing Software 4.14). PDIs of all our samples fall between 0.08 and 0.7, indicating their polydisperse size distribution, making them suitable for the DLS technique. For the DLS analysis the samples were suspended in Mili-Q water in concentration of 0.04 g/l using an ultrasound bath for 10 min, followed by further sonication using an ultrasonic tip (model Sonics & Materials, Inc., Newtown, USA) for another 3 min. Small aliquots of well dispersed powders were subsequently used for the analysis. Determined D_0 values were further used for S_0 calculations as described in article, presented in Chapter 4 (Appendix B, Eq. S4). Real SSAs of the samples (S) were established by the Brunauer–Emmett–Teller (BET) method, using 100-300 mg of the synthesized rutile mesocrystals. First, the samples were degassed in N₂ atmosphere for 4 h at 200 °C. SSAs of the degassed samples were then examined by physisorption measurements of N₂ on the sample's surface using Micrometrics ASAP 2020 analyzer. The particle's morphology (verified by FEG-SEM) was not affected neither by degassing nor by the ultrasonication procedure.

References

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Publications Related to the Thesis

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Biography

The author of this thesis, Vanja Jordan, was born on January 23rd, 1989 in Novo mesto, Slovenia. After graduating from the Technical gymnasium in 2008, she enrolled the Chemical Engineering studies at the Faculty of Chemistry and Chemical Technology at the University of Ljubljana, Slovenia. She completed her bachelor studies in September 2013, with the focus on mathematical modeling of heat transfer and the aim to determine thermodynamic properties that influence the formation of fractal-like crystals in a batch hydrothermal reactor. In October 2013 she enrolled to a doctoral study programme of Nanosciences and Nanotechnologies on the Jožef Stefan International Postgraduate School in Ljubljana, Slovenia. Her PhD topic was fractal-like mesocrystals, produced by the non-classical mesocrystal's growth mechanism, *i.e.* self-assembly. The main focus of her investigation has been to understand the operating mechanism of mesocrystalline rutile's growth and exploit it to control the crystal branching for nanotechnology applications. During her PhD she was awarded with the best oral presentation at the MCM 2015 in Eger, Hungary.