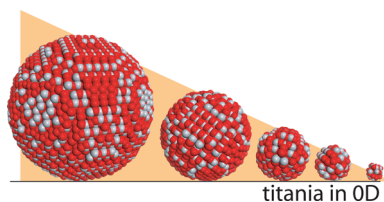# Solution-Phase Synthesis of Titanium Dioxide Nanoparticles and Nanocrystals

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titania in 0D

CONTENTS

1. INTRODUCTION

Titanium dioxide or titania (TiO₂) is one of the most abundant compounds on our planet and a very appealing material for a variety of applications. Unique physical and chemical characteristics combined with earth abundance and nontoxicity, as well as high thermal and chemical stability, make it one of the most employed materials in pigments, UV sunscreens, cosmetics, medical implants, and sensors.[1] In addition to these traditional applications, titania is being employed in many other emerging applications including optoelectronics, photovoltaics, catalysis, fuel cells, batteries, smart windows, and self-cleaning and antifogging surfaces. It is also the most heavily investigated wide band gap semiconductor for photocatalytic and photo-electrocatalytic processes, which have gained increased interest in recent years within the scientific community.[2]

Titania particles and structures possessing small particle and feature size (below 100 nm) can show high visible light transparency combined with high UV light absorption, and in some cases they display iridescence.[3] Small nanoparticles can also enhance the adsorption coefficients of organic molecules adsorbed on their surfaces.[4] In addition, altering the size, as well as the shape, of titania nanoparticles has been shown to strongly influence the adsorption of molecules and the rate of electron transfer events at the particle surface, which has potentially important implications for a variety of applications, including catalysis. As a result, titania particles in the size regime 1−100 nm are very interesting for a variety of technological applications, and the synthesis of well-controlled titania nanostructures is important in order to impart the desired characteristics to the final material. Particle size, shape, and phase are critical in determining the final properties of the nanoscale materials.

Among the many methods used to prepare nanoparticles and nanostructures, a primary classification can be made by distinguishing physical and chemical methods. Physical methods usually rely on top-down approaches in which small structures are fabricated from larger ones. In contrast, chemical methods most commonly proceed through a bottom-up approach, in which molecular precursors react to form the final larger structures. Both methods have advantages and disadvantages: physical methods can produce large quantities of material (e.g., the preferred methods in the electronic industry are physical methods) but their resolution is limited to tens of nanometers. Chemical methods, on the other hand, are typically performed at a smaller scale in which the precision during the preparation of small (e.g., <100 nm and often <10 nm) structures can approach the atomic-layer limit.[5]

Wet chemical or solution-phase methods, in particular, are best suited to achieve the finest control over particle size, shape, and composition as desired for several of the above-mentioned
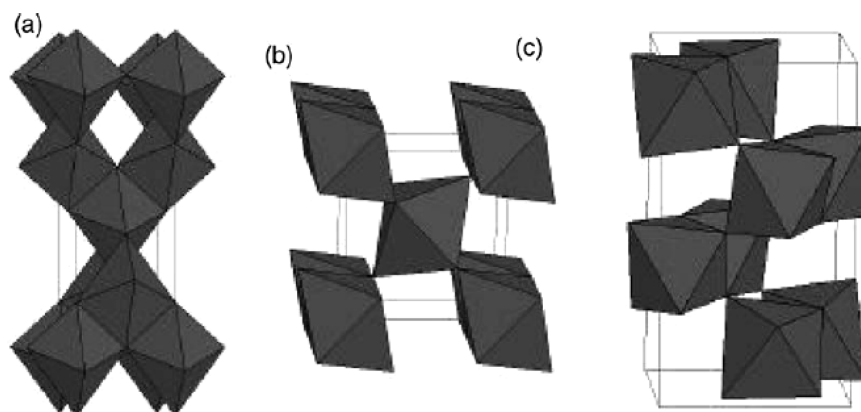
Figure 1. Connectivity of TiO_6^{2-} octahedral units in (a) anatase, (b) rutile, and (c) brookite. Reprinted with permission from ref 15. Copyright 2004 Elsevier.

applications. This control primarily comes from the use of molecular precursors in combination with organic molecules that act as protecting or structure-directing agents in solution and control/limit the growth of the structures. A further advantage of such methods is that the particles often display high dispersibility in common solvents, allowing for the preparation of thin films from concentrated solutions[6] in addition to their use as powders. Nanostructures with complex morphologies can be also achieved by manipulating nanocrystal growth in solution.[7,8] Additionally, recent methods for removing or replacing the long organic ligands with smaller and compact organic or inorganic molecules[9−11] have allowed for the utilization of nanocrystals with controlled morphology in an even broader spectrum of materials science applications than were previously possible.

Titania naturally forms in four main phases: rutile, anatase, brookite, and $TiO_2(B)$. The relative stability of the four titania phases depends on particle size, with rutile being the thermodynamically stable form in bulk titania but anatase being the most stable phase at sizes below 14 nm.[12] Brookite and $TiO_2(B)$ are metastable forms that are not commonly observed in minerals and are difficult to synthesize in pure form. Several polymorphs have been synthesized, including many high-pressure phases.[13] The structural difference between these polymorphs lies in the connectivity of the TiO_6^{2-} octahedral units, which share edges and corners in different ways depending on the crystal phase: generally speaking, anatase forms from octahedra that share four edges; in rutile, two edges are shared; and in brookite, three edges are shared (Figure 1).[14,15] For $TiO_2(B)$, the fundamental building block is similar to the anatase one, with four octahedra sharing edges, but with a different 3D arrangement that produces a layered structure.[13,16] Interestingly, the Ti−O bond distances do not vary much between the different polymorphs, while the O−O distances among shared and unshared octahedral are quite variable. The four polymorphs can be distinguished by X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM) techniques. Due to the similar structure, however, anatase and brookite phases can easily be confused, especially when present as mixtures. In those cases, electrochemical techniques such as cyclic voltammetry can be used to distinguish the different electrochemical response of the polymorphs.[17,18]

Some authors have claimed that the geometry of the titanium precursor in solution can influence the formation of a particular phase, because it influences how the octahedral subunits assemble to form titania. For example, at high pH (basic), the number of OH groups increases, increasing the probability of edge sharing, thus favoring anatase. At low pH, on the other hand, more water molecules are bound to the Ti^{4+} center, thus favoring corner-sharing and formation of the rutile phase.[19] This has been generally observed for aqueous-phase routes to titania, such as hydrothermal synthesis. However, these rules are not strict and the formation of other phases has been reported.[19] To accurately predict the formation of a particular phase, the partial charge model is invoked,[20] which predicts the size of the hydration sphere around cations or anions in solution by assuming that water molecules are "electrostricted" or held in place by the electrostatic field of the ion. Therefore, titanium ions with a different immediate coordination sphere would have a certain number of water molecules electrostricted in the surroundings, and the structure of this ion and of the water molecules associated with it would dictate the formation of one phase over another.

In this review, we summarize the main synthetic techniques used to prepare titania nanocrystals with controlled properties in the nanoscale regime. We limit this review to quasi-zero-dimensional systems, which we define as nearly isotropic nanocrystals (spherical or quasi-spherical) with sizes smaller than 100 nm. Particular focus is given to solution-phase synthesis, which allows exquisite control over many of the parameters cited above. Despite being incredibly important, particularly for industrial applications, titania produced by gas-phase and physical methods is excluded from this discussion.

The review is organized as follows: section 2 reviews nanocrystal synthesis and the use of surfactants in combination with wet chemistry methods; section 3 reports a list of titania precursors along with availability and chemical properties; section 4 discusses aqueous synthetic methods, in particular sol−gel and hydrothermal methods; section 5 is an overview of nonaqueous, surfactant-assisted synthetic methods including solvothermal and nonhydrolytic processes; and section 6 reports templated approaches for titania synthesis. While clear distinctions between several of the solution-phase methods often cannot be drawn due to the blending of various techniques, we attempt to categorize here for the sake of clarity. Table 1 summarizes the synthetic procedures reported in this review.

Table 1. Synthetic Procedures to Prepare Titania Nanoparticles and Nanocrystals with Different Morphologies and Crystal Phases

Ti precursor	product morphology	surfactants or additives	crystal phase[a]	ref
		Sol−Gel Methods		
$TiCl_4$	micrometer-size spheres	HCl, Na_2SO_4	R or R+A	87
titanium butoxide	spheres	HNO_3	A	91
titanium ethoxide	micrometer-size spheres	none	amorphous	88
titanium ethoxide	micrometer-size porous and nonporous spheres	various salts and polymers	amorphous	89
acetylacetone-modified TTIP[b]	spheres	p-toluenesulfonic acid	A	92
$TiCl_4$	irregular spheres	myristic acid	A	93
acetylacetone-modified TTIP	spheres	F127-CTAB[c]	A	94, 95
TTIP	spheres	HCl	R or A	97
TTIP	spheres	NaCl	A	98
TTIP[d]	irregular	diethylene glycol	A	101
titanatrane[e]	spheres or spindles	NH_3	A	104
titanatrane[e]	spindles	amino acids[f]	A	105
$TiCl_4$	irregular	C16mimCl, C4mimBF4[g]	$TiO_2(B)$	106
$TiCl_4$	irregular	several ionic liquids	$TiO_2(B)$	107
		Hydrothermal Methods		
TTIP	irregular	ethanol + HNO_3	A	6
titanium glycolate	irregular	ammonia	B	71, 73
titanium glycolate	irregular spheres	H_2SO_4	B	81
TTIP	irregular spheres	none	R	109
titania powder (rutile)	nanotubes	Na^+	titanate	112,113
titanate nanotubes	nanotubes	Na^+	B	115
titanate nanotubes	nanorods	HNO_3	A	116
titania powder	nanosheets	Na^+	titanate	118
titanate nanotubes	tetragonal rods	none	A	117
lamellar protonated titanate	several, both elongated and compact	H^+	A	119
lamellar protonated titanate	small platelets	HF	A	120
titanate nanotubes	bipyramids, spindles, needles	Li^+, Na^+, or K^+	A	121
$TiCl_4$	irregular	Cl^- (from HCl or NaCl)	B > R	126
$Ti(OH)_4$	several	oxalate, lactate, F^-, acetate, SO_4^{2-}	A, B, or R	128
$Ti(SO_4)_2$, $TiCl_4$, TiF_4, $Ti(OBu)_4$	bipyramids, rods, irregular shapes	hydrazine	A or mixed	129
$(NH_4)_2(OH)_2Ti(C_3H_4O_3)_2$[h]	irregular spheres	none	A	131
$TiOSO_4$	large rods (spindles)	OH^-	B	124
$(NH_4)_2(OH)_2Ti(C_3H_4O_3)_2$	spherical or rodlike	urea	A or B	132
$Ti(OBu)_4$	spheres or truncated bipyramids	HF, H_2O_2	A	133
titanium powder	hierarchical spheres	HF	A	135
$Ti(SO_4)_2$	nanocrystalline powder	HF	A	136
TTIP or TiF_4	nanoplates	HF	A	137
$Ti(OBu)_4$	rectangular plates	HF	A	138
TTIP	tetragonal bipyramids	PVP and acetic acid	A	139
TiF_4	multitwinned microparticles	F^-, EDTA	A	140
lepidocrocite-type $H_{0.68}Ti_{1.83}O_4$	rods	Cs_2CO_3	A	207
$Ti(OBu)_4$[i]	irregular spheres	none	A	141
		Solvothermal Methods		
titanium butoxide	irregular spheres	1,4-butanediol	A	102
TTIP	irregular particles	none	A	148
titanium tert-butoxide	irregular	none	A	149
TTIP	irregular spheres, small rods	oleic acid	A	150
titanium butoxide	tetragonal bipyramids	oleic acid + NaF	A	151
$TiCl_3$ + TiF_4	irregular	none	A	152
$TiCl_4$	faceted crystallites	none	A, A+R	155
amorphous titania powder	small spheres	trifluoroacetic acid	A	159
$TiO(acac)_2$	irregular elongated	sodium laurate	B	160
$Ti(OBu)_4$	spheres and rods	linoleic acid, NH_4HCO_3	A	162
$TiCl_4$[j]	spherical nanoparticles	benzyl alcohol	A	163,164
$TiCl_4$	irregular	poly(1,4-butanediol)	A	166
TTIP	sheets or rhombic	oleylamine, water	A	178
		Surfactant-Assisted Methods		
TTIP	nanorods; hexagonal nanocrystals	tetraalkylammonium cations	A	111
$TiCl_4$ or TiF_4	truncated bipyramids, plates	oleic acid + oleylamine + 1-octadecanol	A	153

Table 1. continued

Ti precursor	product morphology	surfactants or additives	crystal phase[a]	ref
		Surfactant-Assisted Methods		
TiCl$_4$ + TTIP	spherical nanoparticles	oleic acid	amorphous	168
modified TTIP	spherical nanoparticles	TOPO[k]	not reported	169
TiCl$_4$ + titanium butoxide	spherical nanoparticles	TOPO	A	170
TTIP	nanorods or spheres	oleic acid	A	171
TTIP	small spheres or rods	oleic acid + oleylamine	A	172
TiCl$_4$	small rods	oleic acid + oleylamine	A	173
TTIP or butoxide	thin rods	oleic acid + oleylamine	A	174
TiCl$_4$	small particles	ethanol + benzyl alcohol	A	175
TiCl$_4$, Ti(OR)$_4$	small particles	ethanol + benzyl alcohol + water	A	177
titanium thiobenzoate	spherical nanoparticles	benzyl alcohol	A	179
TiCl$_4$	spherical nanoparticles	*tert*-butyl alcohol	A	180
Ti(COT)$_2$	spherical	TBPO[l] + TOPO	B	181
TTIP	spherical nanocrystals	oleic acid + H$_2$O$_2$	not reported	182
TTIP	faceted, cubiclike nanocrystals	[bmim]$^+$[BF$_4$]$^{-\ m}$	A	185
		Microemulsion Methods		
TiCl$_4$	spherical nanoparticles	Triton X-100	amorphous	189
titanium ethoxide	spherical particles	NP-5[n]	amorphous	190
TiCl$_4$	irregular	NP-5 and NP-9	amorphous	191
TTIP	spherical	PFPECOO$^-$ $^+$NH$_4$, PDMAEMA-*b*-PFOMA[o]	amorphous	192
titanium butoxide	elongated irregular	NP-5, acid	R	193
TiCl$_4$[p]	irregular	Triton X-100	A+R	194
titanium butoxide[p]	irregular	Triton X-100	A	195
TTIP	spherical	AOT[q]	A	196
		Templated Methods		
(NH$_4$)$_2$(OH)$_2$Ti(C$_3$H$_4$O$_3$)$_2$	irregular	R5 peptide	amorphous	200
TiF$_6^{2-}$	irregular	fungus *Fusarium oxysporum*	amorphous	201
(NH$_4$)$_2$(OH)$_2$Ti(C$_3$H$_4$O$_3$)$_2$	irregular	protamine	amorphous	202
TiF$_4$	octahedral cages	Cu$_2$O templates	A	203
TiF$_4$	mesoporous single crystals	SiO$_2$ monodisperse spheres	A	205
titanium butoxide	hollow spheres	polystyrene spheres	A	204
TTIP	spherical particles	egg albumen proteins	A	199
TiCl$_4$	small particles	mesoporous silica	A	206

[a]R, rutile; A, anatase; B, brookite. [b]TTIP, titanium isopropoxide. [c]CTAB, cetyltrimethylammonium bromide. [d]Sol−gel (polyol) method. [e]Gel−sol method. [f]Glutamic and aspartic acids. [g]C16mimCl, 1-hexadecyl-3-methylimidazolium chloride; C4mimBF4, 1-butyl-3-methylimidazolium tetrafluoroborate. [h](NH$_4$)$_2$(OH)$_2$Ti(C$_3$H$_4$O$_3$)$_2$, titanium bis(ammonium lactato)dihydroxide. [i]Hydrothermal method in supercritical CO$_2$. [j]Solvothermal method (benzyl alcohol route). [k]TOPO, trioctylphosphine oxide. [l]TBPO, tributylphosphine oxide. [m][bmim]$^+$[BF$_4$]$^-$, 1-butyl-3-methylimidazolium tetrafluoroborate. [n]NP-5, polyoxyethylene-5-nonylphenyl ether. [o]PFPECOO$^-$ $^+$NH$_4$, ammonium carboxylate perfluoropolyether; PDMAEMA-*b*-PFOMA, poly(dimethyl amino ethyl methacrylate-*block*-1H,1H,2H,2H-perfluorooctyl methacrylate. [p]Microemulsion + hydrothermal method. [q]AOT, sodium bis(2-ethylhexyl) sulfosuccinate.

## 2. GENERAL PRINCIPLES FOR SYNTHESIS OF TITANIA PARTICLES

2.1. Solution-Phase Synthesis of Uniform Particles

The process of formation of nanoparticles and nanocrystals is classically divided into two events: nucleation and growth.[21] In the nucleation regime, small clusters composed of a few atoms (nuclei) are formed in the solution starting from monomers, while in the growth regime existing nuclei grow to form larger particles. Besides these two fundamental events, other processes (e.g., Ostwald ripening) can be active during any stage of particle preparation. Precautions must therefore be taken to achieve complete separation between nucleation and growth and to successfully isolate uniform nanoparticles.

The first fundamental event in the preparation of nanoparticles is nucleation. For a given system, there exists a nucleation threshold in terms of the concentration of precursors in solution, above which nuclei will spontaneously form. Thus, nucleation is driven by a supersaturation stage in which the concentration of reactive monomers overcomes this

critical nucleation concentration. This process is usually induced by fast decomposition of the metallic precursor or by a sudden variation in the concentration of a reactive species that is critically involved in the chemical mechanism of particle formation. The choice of the precursor is thus very important because it determines the energetic pathway by which a monomer is activated into the active species.

When supersaturation is relieved by the formation of nuclei, the system enters the growth stage, in which no additional nuclei are formed but only existing clusters grow larger (Figure 2).[22] The growth can be obtained through two main mechanisms: monomer addition from solution or Ostwald ripening. In the first case, the adsorption of a monomer onto the formed nuclei and its decomposition induces the growth. In the second case, the high surface energy of small nanocrystals allows for them to redissolve (in the presence of ligands/adsorbed species), releasing new monomers into solution that can then redeposit onto the surface of the larger particles. It is known that if the growth of the nanocrystals occupies a large fraction of the synthesis time, these Ostwald ripening or other

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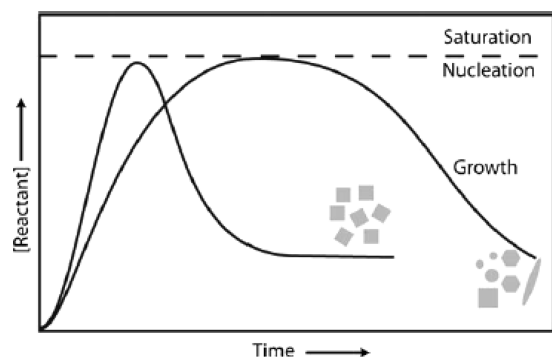
Figure 2. La Mer model for nucleation and growth kinetics of nanoparticles. A narrow size distribution is favored when a fast, single nucleation event occurs, leading to nanocrystals with very similar growth processes. Reprinted with permission from ref 22. Copyright 2008 Wiley–VCH.

etching processes (digestive ripening, essentially an induced Ostwald ripening process) can allow the uniformity to be improved in a process that is usually referred to as size-focusing.[23,24]

The temporal separation between nucleation and growth is achieved through "burst nucleation," a concept typically invoked in the solution-phase synthesis of nanoscale materials (larger particles require a different theoretical treatment).[25] In this process, supersaturation is achieved and relieved in a very limited time window, such that the nuclei form almost simultaneously and enter the growth stage soon after they are formed. Initial attempts to prepare monodisperse nanocrystals relied on the injection of one or more of the precursors at high temperature (hot-injection) to produce the burst nucleation by achieving a very high monomer concentration in a few seconds[26] (Figure 2). It has since been found that uniform nanocrystals can be produced by heating-up methods, in which burst nucleation is achieved after the rapid decomposition of precursors at a specific temperature.[27]

In a variation, seeded-growth approaches can be used to prepare large nanocrystals or particles with different morphologies by temporally separating nucleation and growth. In this method, a solution of precursors/monomers is added to preformed nuclei at an appropriate (usually low) rate to suppress nucleation in solution and maintain monomer concentrations within the growth regime.[28,29]

The processes described above adhere to the classical La Mer theory, but other unconventional processes including oriented attachment are also well-known in the synthesis of nanocrystals.[30] Since these processes do not usually play a central role in the preparation of zero-dimensional (0D) nanocrystals, we address the reader to excellent reviews on this topic.[31–33]

## 2.2. Surfactants and Protecting Ligands

Small crystals (e.g., <50 nm) are typically unstable in solution because they possess a large number of surface atoms, driving them to agglomerate into larger structures to minimize surface energy. Therefore, in order to prepare small particles, surface stabilizers must be used to prevent agglomeration and to impart solubility. Stabilization with ligands can be obtained by introducing either steric or electrostatic interactions (or both) that keep the particles separated. Steric repulsion is obtained from long-chain ligands or polymers that passivate surface atoms, thus reducing free surface energy, and keep the central inorganic cores from fusing together through the formation of

an "insulating" organic layer on the metal surface. Electrostatic repulsion is obtained by forming an electrical double layer of ions around the nanocrystals, which results in repulsion between the charged particles. Organic ligands and polymers that contain hydrolyzable groups provide both steric and electrostatic stabilization simultaneously.

In addition to providing stabilization of the inorganic core, surfactants and capping ligands also play an important role in dictating the preferential growth of specific facets forming anisotropic structures or in influencing the electronic properties of the particles (e.g., in semiconductor quantum dots).[34] In titania, studies have revealed that the ripening and oriented attachment of particles can be influenced by the adsorption of certain ligands onto specific facets.[35] The choice of surfactants is therefore critical in determining and imparting the appropriate characteristics to the final nanocrystal product.[36] In the case of synthetic approaches in solution, the organic monolayer must also act like a "living interface", as it should allow nanocrystal growth while preventing severe agglomeration. Additionally, a specific ligand can be selected at different steps in the reaction; for example, during ligand exchange a molecule is chosen that binds the inorganic core more strongly than the existing ligand in order to drive the process forward.

Many different organic molecules can be used as surfactants and protecting ligands for nanocrystal synthesis. The most commonly used functional groups are carboxylic acids, alcohols and diols, amines, thiols, phospines, and phosphonic acids. The surfactant heteroatoms typically bind to the nanocrystal surface atoms while the alkyl groups exposed on the surface impart solubility and colloidal stability to the growing crystal. The choice of surfactant depends first of all on the type of material that is prepared. Because of the chemical nature of different atoms, some materials form stronger chemical bonds with one specific organic group more than another. As a classical example, the Brust synthesis of Au nanoparticles was made possible by the use of thiols which bind very strongly Au surfaces, therefore limiting the growth of Au nanoparticles to very small sizes.[37]

Titania is composed of "hard" Ti(IV) cations that correspondingly bind hard ligands, in particular oxygenated ones. Carboxylic acids and diols are therefore usually strong ligands for titania, as demonstrated for the {001} facets of anatase, onto which both functional groups adsorb dissociatively.[4,38,39] Jun et al.[35] studied the influence of the concentration of lauric acid in the shape evolution of anatase crystallites and found that this surfactant binds very strongly to the {001} facets, resulting in the inhibition of growth along that facet, while trioctylphosphine oxide is essentially noninteracting. Interestingly, the mechanism of coarsening and oriented attachment of titania particles in organic solvents seems to be very similar to what is observed under hydrothermal conditions.[40] Given the commercial availability and low cost of carboxylic acids, they are the preferred surfactants used for titania nanocrystal synthesis. Clearly, other organic molecules can be more effective in chelating titanium atoms,[41] but they may not be as readily available. In this respect, carboxylic acids can serve the dual function of protecting agents and also modifiers to slow down the formation of the titania lattice. As a way to catalyze the formation of the final bond network, other compounds are used during the synthesis, such as ammonia in the case of hydrothermal procedures or primary amines for reactions involving organic solvents.
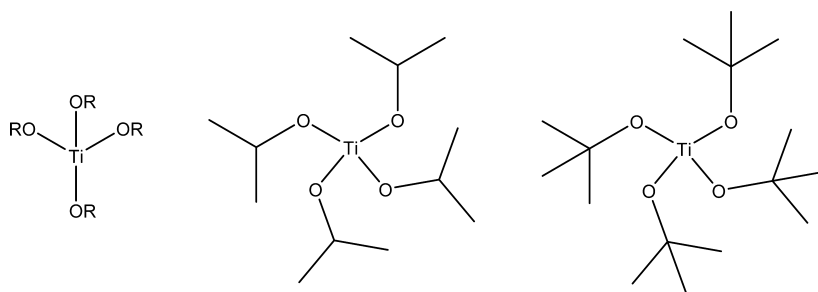
Figure 3. General structure of a titanium alkoxide (R = organic groups, left), and of two commercially available and popular titanium alkoxides, titanium tetraisopropoxide (TTIP, center) and titanium *tert*-butoxide (right).

Another interesting class of organic compounds that can be used as ligands for nanoparticles and nanocrystals are polymers. The wide availability of polymers and copolymers with a range of functional groups represents an exciting way to tailor the solubility and functionality of inorganic nanostructures.[42] Furthermore, polymers can allow the organization of nanocrystals into hierarchical architectures with precise control over the position of subunits.[43] Among the most commonly employed polymers for titania synthesis are those containing oxygenated and amino groups such as poly(acrylic acid) (PAA), poly(methyl methacrylate) (PMMA), poly(vinylpyrrolidone) (PVP), and poly(amido)amines.[44] Furthermore, inspired by biomimetic approaches that organisms and plants employ to produce inorganic materials such as silicates,[45−47] several other polymers have been prepared with amine, carboxylic, and hydroxyl groups that can be used as ligands during titania synthesis.[48]
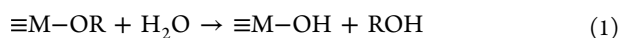
3. TITANIUM PRECURSORS

There is a wide availability of titanium precursors, both organic and inorganic, that are useful in the preparation of titania nanocrystals. In this section we report a list of the most commonly used precursors in titania synthesis and some of their properties.

3.1. Titanium Alkoxides

Alkoxides are compounds with general formula $Ti(OR)_4$, with R representing an organic group. The most common (and commercially available) titanium alkoxides are titanium isopropoxide [TTIP; R = $CH(CH_3)_2$], titanium butoxide (R = $CH_2CH_2CH_2CH_3$), and titanium *tert*-butoxide [R = $C(CH_3)_3$] (Figure 3).

Titanium alkoxides are among the most used precursors in the preparation of titania nanocrystals, particularly in the sol−gel method, because of their versatility and well-studied chemistry.[49] They are very reactive due to the Lewis acidity of the Ti(IV) center, which makes it very susceptible to nucleophilic attack, for example by water. The mechanism of the hydrolysis of titanium alkoxides depends on the reaction conditions, in particular on pH, but it generally involves the nucleophilic addition of a water molecule onto the Ti center followed by proton transfer from the water molecule to a coordinating ligand during a transition state, and the final removal of the protonated ligand in the form of an alcohol molecule. The fully hydrolyzed product is $Ti(OH)_4$.[50] However, under controlled conditions, hydrolysis and condensation result in the formation of Ti−O−Ti bonds from alkoxides through the following reactions (eqs 1−3):[51]

$$\equiv M-OR + H_2O \rightarrow \equiv M-OH + ROH \qquad (1)$$

$$\equiv M-OH + HO-M\equiv \rightarrow \equiv M-O-M\equiv + H_2O \qquad (2)$$

$$\equiv M-OR + HO-M\equiv \rightarrow \equiv M-O-M\equiv + ROH \qquad (3)$$

The theoretical coordination number of the Ti center in common alkoxides is 4, but it can easily expand to 6 through the formation of oxo bridges or complexes. Being highly reactive toward water, titanium alkoxides are very sensitive to humidity and must be carefully handled to avoid premature hydrolysis, which can compromise the synthesis. Advantageously, for the same reason alkoxy groups can be easily replaced by diols, β-diketonates, carboxylic acids, amines, or other organic groups such as cyclooctatetraene (COT),[52] resulting in the formation of complexes whose reactivity can be better tailored and controlled. These complexes are often polynuclear, with the nuclearity depending on the reaction conditions, and have been studied in detail because of their potential use in several other applications, including chemical vapor deposition (CVD) procedures.[53] These modified precursors can show markedly different reactivity than the parental alkoxides in sol−gel-type reactions.[54] Furthermore, they can alter the condensation pathway, leading to the formation of different phases by guiding the bonding of the octahedral TiO_6 units.

3.2. Titanium Halides ($TiCl_4$ and TiF_4)

$TiCl_4$ is obtained in high purity as intermediate compound after thermochemical treatment of upgraded titanium-containing ores with chlorine gas and carbon. It is subsequently oxidized at high temperature in the gas phase to obtain high-quality titania.[55] $TiCl_4$ is very reactive to water and oxygen, forming titanium hydroxide and releasing HCl and Cl_2 gases, respectively, and must therefore be handled carefully. TiF_4 is a more stable compound that can be handled under standard conditions. Although also commercially available, $TiCl_3$ and TiF_3 are much less commonly used in the synthesis of titania nanocrystals. $TiCl_3$ is well-known, however, because of its use for the preparation of polyolefins (Ziegler−Natta catalyst).

$TiCl_4$ is widely used for titania synthesis. In sol−gel and hydrothermal reaction conditions, it easily undergoes hydrolysis in contact with water, forming titanium chlorohydroxy complexes and titanium hydroxide and releasing HCl. It is also used in nonhydrolytic types of synthesis. This precursor is suitable for these reactions because chloride is a good leaving group in nucleophilic substitution-type reactions. Two main reactions produce titania from nonhydrolytic cleavage of the Ti−X bond: the alkoxide route (eq 4) and the ether route (eq 5):[56]

$$MCl_n + M(OR)_n \rightarrow 2MO_{n/2} + nRCl \qquad (4)$$

$$MCl_n + (n/2)ROR \rightarrow MO_{n/2} + nRCl \qquad (5)$$
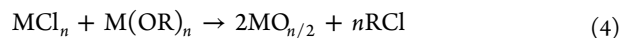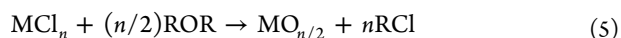
Both reactions are very slow at room temperature, and generally temperatures between 80 and 150 °C are required to obtain reasonable rates and crystalline products. NMR studies revealed that numerous reactions are involved, with an initial redistribution of the ligands around the titanium centers and the formation of intermediate oxochloroalkoxides that autocatalyze the reaction.[56] Furthermore, the ether route was found to lead to a faster formation of the gel compared to the alkoxide route.

TiF_4 has seen much less use in titania synthesis until recently, since there has been a burst of interest in the preparation of anatase titania particles with exposed {001} high-energy facets.[57] These facets, which represent a small percentage of the entire exposed surface in the most thermodynamically stable morphology of anatase, have been suggested as potentially more reactive than the {101} facets that usually dominate in anatase nanocrystals.[58,59] It has been found that fluoride can strongly bind the {001} facets at the exposed 5-fold coordinated Ti cations, reducing their surface energy and allowing growth to occur on the {101} facets.[57,59] Most of the early syntheses utilized HF as the structure-directing agent, but HF is very corrosive and dangerous to handle. TiF_4, on the other hand, is a stable compound that has been postulated to dissociate at high temperature in the presence of carboxylic acids into HF and titanium complexes, similarly to what is observed with $TiCl_4$.[60−62]

3.3. Titanatranes

Atrane compounds are metal complexes that are formed by complexation of a metal or semimetal with triethanolamine. Common atranes include those of silicon, tin, and phosphorus. Titanium atranes (titanatranes) were first described some time ago[63] but have only been studied in detail in the last two decades[64,65] in connection with their potential use in the preparation of fine titania particles,[66] homogeneous catalysts,[67,68] and mesoporous materials.[69] Triethanolamine acts as a chelating ligand, with the three alkoxy groups coordinating to the central atom and incorporation of a transannular N−Ti bond. This type of bonding results in high stability toward hydrolysis. In addition, the ability of triethanolamine to chelate with the titanium center helps to displace ligands present in common titanium precursors, such as alkoxide groups, halides, and amides. The preparation of titanatranes from these precursors is thus straightforward. Figure 4 reports the
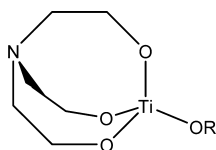
Figure 4. Scheme of a monomeric titanatrane derived from a titanium alkoxide (where R is an organic group).

simplistic structure of a monomeric titanatrane; in many cases, the triethanolamine ligand can act as a multidentate ligand (depending on the Ti/triethanolamine ratio), resulting in the formation of oligo- and polymeric atranes.[70]

3.4. Titanium Metal and Carboxylate-Derived Compounds

Titanium metal is resistant to dilute acids but it can be dissolved in NH_3/H_2O_2 mixtures to form a titanium oxohydroxy complex. This compound is then amenable for further modification with hydroxy acids such as glycolic acid[71] or citric,[72] malic, tartaric, or lactic acid (see below).[73,74]

3.5. Titanium(IV) Bis(ammoniumlactato) Dihydroxide

This precursor of formula $(NH_4)_2(OH)_2Ti(C_3H_4O_3)_2$ is a water-soluble compound that is more stable toward hydrolysis than the common alkoxides due to the chelating lactate group. The Ti ion possesses an octahedral coordination in this compound, which also accounts for its higher stability compared to titanium alkoxides. It is commercially available and is purchased as an aqueous solution at a pH of about 8. It can be hydrolyzed in the presence of strong acids or bases to form TiO_2, in addition to NH_3 and lactic acid (or lactate salts) as byproducts. It has also been employed for the preparation of nanocrystalline titania thin films.[75−77]

3.6. Titanium Sulfate and Oxysulfate

Titanium sulfate $[Ti(SO_4)_2]$ can be obtained in large quantities by dissolving titania ores (such as ilmenite and rutile) with H_2SO_4.[55] It is a water-soluble precursor that has been shown to produce all the three titania polymorphs under hydrothermal conditions, with a preference for anatase.[78] Complexation with oxalate produces rutile powders at room temperature or brookite by decomposition at 300 °C. Titanium oxysulfate $(TiOSO_4)$ has been shown to produce pure anatase powders by precipitation with NaOH at pH 4−6.[79]

### 3.7. Oxobis(2,4-pentanedionato-O,O′)titanium [TiO(acac)₂]

This compound is commercially available and stable in water and is used in hydrothermal preparation of titania powders.[80,81]

4. AQUEOUS METHODS

When titania is prepared through aqueous methods, as in the case of most transition metal oxides, the Ti−O−Ti bond network is formed in two steps: hydrolysis and condensation.[82] The hydrolysis step results in the formation of a metal complex with water in the form of aquo, hydroxo, or oxo complexes, depending on the metal cation and the reaction conditions. Condensation is the reaction between two (or more) of the formed complexes to give the Ti−O−Ti bonds, which are the precursors of the final oxide network. After condensation, oxolation can also occur with the formation of additional oxo bridges between metal fragments through nucleophilic addition. Usually this step is accompanied by water elimination, so that the final Ti−O−Ti bond is formed. These two processes can show very different rates at different pH values. For example, at neutral pH, condensation rates are much faster than hydrolysis rates by 4 orders of magnitude, so that condensation occurs as soon as titanium precursors are hydrolyzed. Under certain conditions, however, these processes can be slow such that catalysts are often added to promote the formation of the bonding network. Commonly used catalysts are acids and bases that promote hydrolysis by either increasing dehydroxylation (a water molecule is removed from a Ti−OH group) or deprotonation (a OH⁻ attacks a Ti center to form a Ti−OH bond). A salt formed by pairing a weak acid and base can also work as a condensation catalyst, as shown in the case of ammonium carbonate or ammonium acetate.[83]

4.1. Sol−Gel Methods

Sol−gel methods are widely used to prepare ceramic materials such as metal oxides, nitrides, and carbides.[84,85] The process involves the transformation of a sol into a gel, which is then usually thermally treated to obtain the final material. Sols are solutions of the precursor compounds (either inorganic or
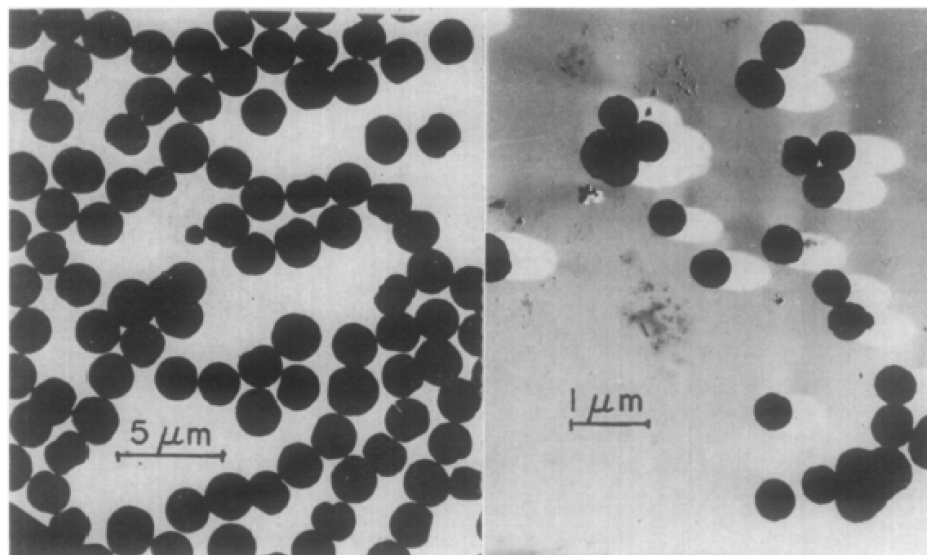
Figure 5. Electron micrographs of rutile titanium dioxide sol particles obtained by sol–gel synthesis at different ratios of $TiCl_4/HCl/Na_2SO_4$. Reprinted with permission from ref 87. Copyright 1977 Elsevier.

metal–organic), which in the case of titania are typically transparent. Following a series of chemical reactions and/or thermal treatments, the precursors react to form a network of bonds, resulting in a solid skeleton of metal–oxygen bonds within a continuous liquid phase. At this point the structure is called a gel. Gels can also be formed by particulate materials, when attractive dispersion forces cause the particles to stick together, forming a continuous network. As this process occurs in the presence of water, the hydrolysis and condensation reactions generally occur very fast and the control over the size, shape, and dispersibility of the particles is thus poor. Furthermore, sol–gel processes usually result in materials that are amorphous or poorly crystalline because they are produced at or near room temperature, although some methods have been developed that avoid this issue.[86] Therefore, a thermal treatment is generally needed to transform the dried gel into the final desired material. For this reason, these methods also do not typically result in stable colloidal particles. However, they have inspired many variations that do provide colloidally stable particles, as for example in the gel–sol method.

In early examples, titania particle size obtained through this method was several hundreds of nanometers. For example, Matijević et al.[87] described the preparation of uniform titania spheres by hydrolysis of $TiCl_4$ in highly acidic solutions (through addition of HCl) containing sulfate ions and then aging of this solution for long periods of time (days or weeks) (Figure 5).

These authors were able to prepare rutile-phase spheres at low sulfate/titanium ratios and mixed rutile–anatase phase spheres at higher ratios. A mechanism of particle size control was described by the authors in terms of the rates of hydrolysis and condensation. At high pH, hydrolysis was too fast and produced particles with poor uniformity. On the other hand, under the highly acidic conditions used in the study, hydroxylation could occur only at elevated temperatures, such that the reaction could be controlled efficiently at room temperature. Furthermore, they observed that the presence of sulfate ions was critical during the formation of uniform particles, but sulfate was not present in the final products. The authors propose that these ions bind strongly to titanium ions

during growth, therefore limiting the hydrolysis rate and providing a constant concentration of monomers in solution, which lead to uniform, linear growth at elevated temperature.

Similar uniform micrometer-size particles were prepared by Barringer and Bowen[88] through the fast hydrolysis of titanium ethoxide or isopropoxide precursors. The most important step in their preparation was the promotion of homogeneous nucleation during hydrolysis and uniform growth of the nuclei by guaranteeing colloidal stability to the growing particles. If small particles flocculated during the growth stage, this produced multinuclear particles that were nonuniform. The uniform particles could be self-assembled into ordered superlattice structures by sedimentation, which displayed interesting iridescent properties when organized in cubic close-packed arrays. Porous and nonporous monodisperse spheres were reported more recently by a similar procedure but with addition of polymers to promote the pore formation.[89]

More recently, titania particle size was controlled in smaller size regimes. Morales et al.[90] studied the hydrolysis of titanium ethoxide in the presence of hydrolyzing agents. These authors investigated the consequences of adding several acids and bases as additives during the synthesis and found some contradictory results. Use of HCl at mild acidic pH resulted in the isolation of crystalline particles containing all three phases of titania. On the other hand, use of oxalic acid or ammonium hydroxide caused the formation of mainly amorphous titania phase. In another report, in the presence of 0.1 M HNO_3 and titanium butoxide, 3.3 nm anatase particles are obtained.[91] By use of HCl at higher concentration, elongated rutile particles were formed. The acidity of the medium and the counterions are therefore equally important for development of the desired particle size and shape. It is, however, hard to explain the preparation of titania of one phase versus another: the many parameters involved in the synthesis do not allow a straightforward prediction.

One of the main problems faced in sol–gel chemistry is proper control of the hydrolysis and condensation rates of titanium precursors, which are usually too fast because of the presence of water and catalysts in solution. An attractive way to overcome this issue is to modify the precursor with complexing ligands that reduce the hydrolysis rate. Scolan and Sanchez[92]
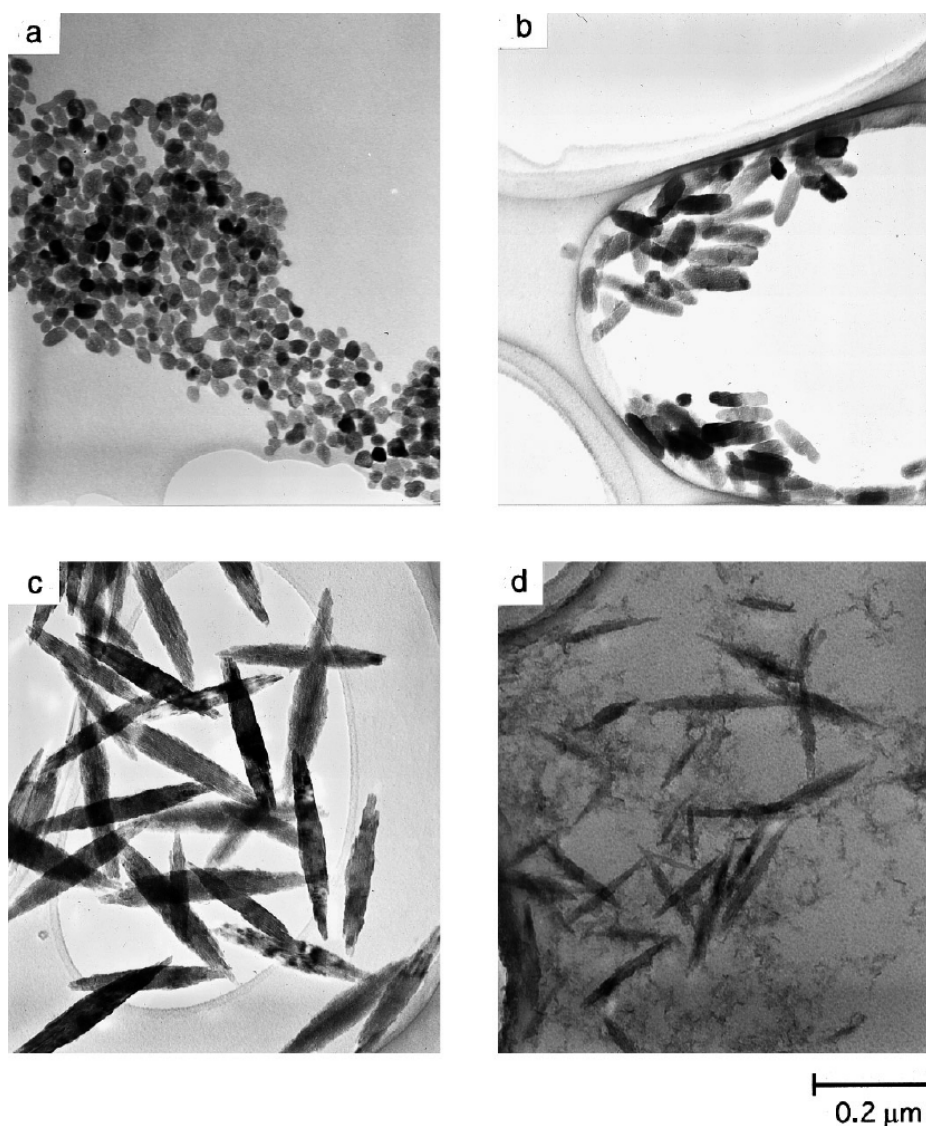
Figure 6. Effect of ammonia concentration on the shape and size of TiO$_2$ particles prepared by a gel−sol method. Ammonia concentrations in suspension were (a) 0, (b) 0.50, (c) 1.0, and (d) 2.0 M, where the initial pH values were (a) 9.5, (b) 10.8, (c) 11.3, and (d) 11.6 at room temperature. Reprinted with permission from ref 104. Copyright 1997 Elsevier.

used acetylacetone as such a ligand and conducted the hydrolysis in the presence of p-toluenesulfonic acid to obtain crystalline, dispersible anatase nanoparticles (1−5 nm). The dispersibility of the resulting particles in water−ethanol mixtures was promoted by the surface capping of acetylacetonato ligands and a mixed layer of p-toluenesulfonic acid and water molecules, as demonstrated by solid-state NMR. Khanna et al.[93] similarly used myristic acid to prepare 5 nm anatase nanocrystals with colloidal stability. Jiu et al.[94,95] used a combination of the surfactants F127 and CTAB to drive the hydrolysis of TTIP modified by acetylacetone. However, in this case, anatase particles of 3−5 nm in size were obtained only after calcination at 450 °C to promote crystallization.

In order to improve the crystalline morphology of sol−gel-prepared particles while avoiding high-temperature postsynthetic treatments such as calcination, which typically preclude colloidal stability, several methods have been reported including ultrasound irradiation[96] and dissolution−precipitation procedures with aging at temperatures between 25 and 220 °C.[97] Another interesting strategy consists of the addition of salts and

polymers to improve crystallinity and crystal shape and structure control. As reported by Han et al.,[98] hydrolysis of TTIP in a solution of NaCl and Pluronic P123 produced anatase nanocrystals of about 6 nm in size that were nonaggregated and crystalline. The use of CH$_3$COOH as catalyst produced anatase nanorods while HCl resulted in rutile particles, in agreement with other studies cited above.

The polyol method has emerged in recent years as a suitable alternative to the sol−gel method to obtain crystalline particles at moderate temperatures. Initially developed for metal and alloy nanoparticles, it was then extended to oxides[99] and is based on the reaction between a polyalcohol and a metal salt. Amorphous niobia and niobium double oxides were among the first oxide materials prepared with this method.[100] More recently, titania particles were prepared by this method by first heating TTIP in diethylene glycol (DEG) at 140 °C, followed by addition of water and increasing the temperature up to 180 °C, resulting in irregular anatase crystallites 30−200 nm in size that exhibited dispersibility in DEG.[101] Similarly, titanium butoxide was thermally decomposed in 1,4-butanediol at 300
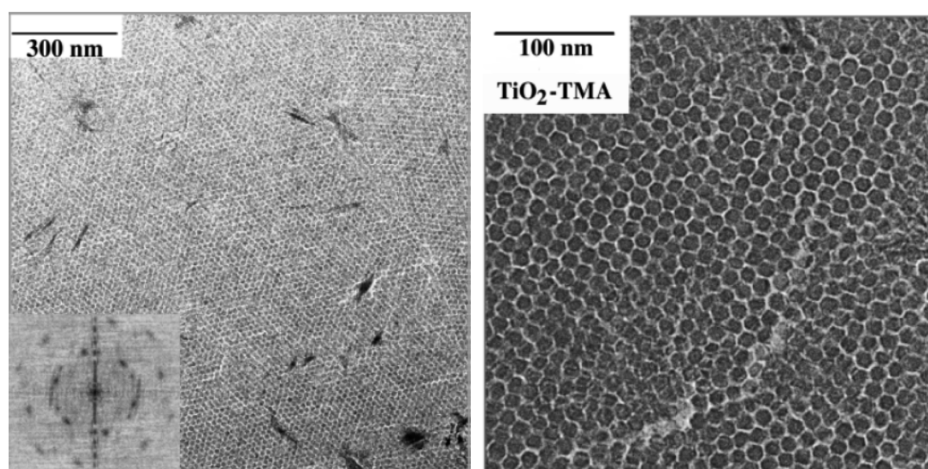
Figure 7. (Left) Transmission electron micrograph of titania/Me$_4$N$^+$ nanocrystals self-assembled into a superlattice with dimensions on the order of micrometers; the power spectrum (inset) confirms the long-range translational and orientational order of the superlattice. (Right) High magnification shows well-faceted hexagonal nanocrystals. Reproduced with permission from ref 111. Copyright 1999 Wiley−VCH.

°C to yield anatase particles of 15 nm.[102] However, the particle size and shape was not much controlled.

In another variation of the classical sol−gel method, in the early 1990s Sugimoto and Sakata[103] developed the so-called "gel−sol" method. Originally applied to the preparation of α-Fe$_2$O$_3$ particles,[103] it is based on the preparation of a metal hydroxide gel that is then aged to obtain a sol in which colloidal particles are dispersed. By this technique, colloidal dispersions of titania particles can also be produced. To do that, these authors started with a titanium−triethanolamine complex (titanatrane) that was useful to slow the hydrolysis rate. The complex was dissolved in aqueous ammonia and heated at 100 °C to form the initial gel composed mainly of titanium hydroxide. No titania formation was observed up to this point. The gel was then aged at 140 °C for 3 days, producing anatase particles with roughly spherical or spindlelike morphology depending on the pH of the initial solution (Figure 6).[104] These authors stated that ammonia (or primary amines) acted as the shape-directing agent, causing elongation of the particle by adsorption onto the crystal planes parallel to the c-axis of the particles. However, higher concentrations of ammonia inhibited the formation of particles, probably because of the formation of solution titanium hydroxide aquo complexes. This is related to the mechanism of anatase formation, which is postulated to start from a Ti(OH)$_3$$^+$ intermediate that reacts with Ti(OH)$_4$ to form TiO$_2$; at high ammonia contents, the concentration of Ti(OH)$_3$$^+$ species is too low to induce nucleation by this pathway.[50] In an extension of the same procedure, these authors demonstrated shape control by using different amino acids as protecting ligands; in this case, elongation along the c-axis was promoted by glutamic or aspartic acid.[105]

Sol−gel methods have been reported to provide access to the TiO$_2$(B) phase. In particular, the use of ionic liquids with tetrafluoroborate ions efficiently produced phase-pure TiO$_2$(B) particles in good yield.[106] However, these particles are not well dispersible but rather agglomerated to form mesoporous secondary particles consisting of smaller ones. Although the initial procedure claimed that the concentration of BF$_4$$^-$ ions was crucial for obtaining TiO$_2$(B) phase, a more recent report showed the ionic liquid concentration to be a more important parameter.[107] The authors then postulated that the interactions between titanium ions in solution and ionic liquid molecules can induce the formation of micelles that induce the formation of titania in the TiO$_2$(B) polymorph.

As mentioned in the Introduction, sol−gel methods are easy procedures to obtain titania particles in solution. However, poor crystallinity and control over phase and size distribution prompted researchers to study alternative methods of synthesis. One of these methods is hydrothermal, which is presented in section 4.2.

4.2. Hydrothermal Methods

Similarly to sol−gel methods, most hydrothermal approaches do not provide materials with tailored properties such as solubility, uniformity, and processability. In particular, in the absence of surfactants/protecting agents, the resulting particles are generally not soluble in common polar or apolar solvents. Nevertheless, the crystallinity of the particles is usually much improved compared to sol−gel methods, and for some applications where dispersibility is not required, these materials can be very useful, and hydrothermal methods require few steps. Typically, bases such as ammonia or alkaline hydroxides are employed to form a titanium hydroxide intermediate, which is then dehydrated to titania under the applied hydrothermal reaction conditions at relatively high temperatures (usually between 150 and 250 °C). Several factors, such as pH, temperature, presence of "mineralizers" (typically, inorganic compounds that are claimed to be important for the preparation of several materials by mechanisms that are not well understood),[108] and stirring[109] of the solution are pivotal in controlling not only the morphology of the crystallites but also the phase. Reaction time is also important in determining the final morphology of the particles, as the crystals can proceed through intermediate, metastable states before reaching the final equilibrium morphology.[110]

In one of the earliest attempts to manipulate titania crystal shape by hydrothermal methods, Chemseddine and Moritz[111] hydrolyzed titanium alkoxide in the presence of quarternary ammonium hydroxide bases to obtain anatase crystals with hexagonal, rectangular, and rodlike morphology. A precipitate was obtained after reaction of titanium alkoxide with water and base at room temperature, which was then redissolved after reflux of the solution, and titania particles eventually formed. Formation of anatase crystals was rationalized on the basis of a number of steps including hydrolysis, condensation, and
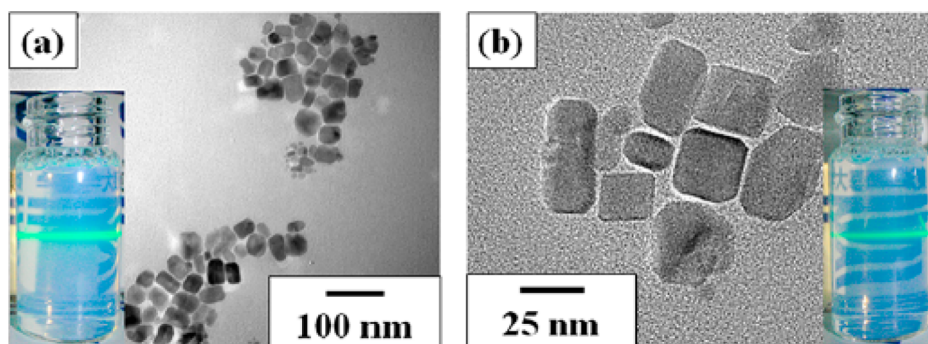
Figure 8. TEM images of brookite nanoparticles dispersible in both hydrophilic and hydrophobic environments such as (a) water and (b) cyclohexane, synthesized by hydrothermal treatment in the presence of sodium oleate. Inset photographs show that the synthesized nanoparticles exhibit excellent dispersibility in both solutions. Reprinted with permission from ref 123. Copyright 2012 American Chemical Society.

polymerization of the several titanium−oxygen species that are formed during the reaction. These authors argue that the basic building unit consisted of octahedral clusters where titanium atoms were coordinated to six oxygen species (similar to the basic structure of titania polymorphs reported in the Introduction). These clusters then share oxygen corners in a manner determined by the nature of the oxygen groups and the presence of stabilizing molecules. The stabilizing role of quaternary ammonium cations on the {101} facets was evident from the fact that by increasing the concentration, these authors were able to grow the particle along the [001] direction, resulting in rodlike structures. At an appropriate alkoxide/base ratio, very uniform, well-faceted hexagonal nanocrystals were formed that self-assembled to give 2D superlattices (Figure 7).

Another early example of shape control via hydrothermal treatment is the preparation of titania nanotubes by treating titania powders in 10 M NaOH at 110 °C.[112,113] The nanotubes are ~8 nm in diameter and >100 nm in length, and recent studies revealed that the crystal structure is more properly described as a titanate phase.[114] Na+ (and H+) ions were postulated to direct the formation of the tubular structures by stabilizing the $[TiO_6]$ octahedral layers that are produced during the synthesis.[115] Interest in titanate nanotubes arises from the fact that they are widely used as precursors for other structures under hydrothermal conditions. For example, anatase titania nanorods,[116,117] very thin sheets,[118] or a variety of elongated or compact shapes have been reported by transforming titanate nanotubes at different temperatures and pH, and with different additives.[119] Similarly, lamellar protonated titanates, in combination with HF, can be converted into small anatase crystals with a platelet morphology and exposed {001} facets.[120]

A recent investigation analyzed the effect of alkali salts on the shape of titania particles prepared by a hydrothermal process starting also from titanate nanotubes.[121] The particles were all anatase but the samples prepared in the presence of lithium ions exhibited a bipyramidal shape, while use of larger alkali ions like sodium and potassium caused the particles to evolve into more elongated, needlelike shapes. High-resolution (HR) TEM analysis suggested that the growth of the structures occurred along the ⟨001⟩ direction and exposed the {301} facets. The authors rationalized this result by invoking a mechanism in which small, positive Li+ ions interact with surface and subsurface oxygen atoms in the lattice, slowing down the growth rate of all facets and resulting in low aspect ratio particles. In contrast, large K+ ions interact favorably only with the top oxygen atoms, resulting in faster growing rates in

the ⟨001⟩ direction and leading to subsequent {301} facets exposed in the final products.

Hydrothermal treatments can also be used to transform the titanate nanotubes into pure brookite nanocrystals in concentrated (2 M) $HClO_4$ solution.[122] The acid anion was found to be important in determining the final phase of the material, as Cl− and NO_3^- induced the formation of rutile rather than brookite after prolonged hydrothermal treatments. However, Deng et al.[115] reported a similar procedure but claimed that only under strongly basic conditions did the anatase tubes convert into pure phase brookite, in the presence of Na+ cations. Brookite particles were also obtained starting from a titanium glycolate complex and using H_2SO_4 under hydrothermal conditions.[81] It was found that the concentration of the acid played a key role in the formation of pure brookite particles; rutile was favored at lower concentrations and anatase at higher ones.

Brookite nanoparticles were obtained by starting with titanium glycolate and using sodium oleate as an additive during the synthesis.[123] The particle phase was particularly sensitive to the amount of additive in the synthesis: a relatively low or high amount favored anatase formation, while brookite was produced at intermediate concentrations of sodium oleate. The particles obtained in this way were dispersible in both polar and nonpolar solvents (Figure 8), probably due to the formation of a sodium oleate double layer that allowed the particles to switch from hydrophobic to hydrophilic monolayer coating depending on the conditions, as proven by ζ-potential measurements.

Basic hydrothermal conditions generally favor the formation of brookite nanoparticles. Large brookite rods (length ~300 nm and diameter ~50 nm) were prepared by hydrothermal treatment of $TiOSO_4$ in the presence of sodium hydroxide.[124] Pure brookite particles were also prepared by hydrothermal treatment of a particular titanium glycolate−peroxo complex whose crystal structure resembled that of brookite base units.[71] Indeed, in a series of experiments these authors found that the only hydroxycarboxylic acid that resulted in brookite was glycolic acid at pH 10.[73]

When $TiCl_4$ is utilized as a titanium precursor under hydrothermal conditions, very different titania materials can be obtained, the morphology and phase of which depends on the synthesis parameters. When $TiCl_4$ is reacted with water, the species $[Ti(OH)_nCl_m(H_2O)_{6-n-m}]^{(n+m-4)-}$ is present in solution, with n and m depending on the conditions. An interplay exists between solution pH, presence of counterions, and temperature, which determines the nature of the titanium

complex in solution that is transformed into titania. pH directly affects n, while the concentration of Cl^- (for example, by addition of a second source of this anion) directly influences m. At moderately acidic pH, rutile particles can be prepared and addition of Cl^- (by addition of NaCl) results in anisotropic growth, yielding rods.[125] In highly concentrated HCl solutions, $TiCl_4$ is likely transformed into the neutral molecule $Ti(OH)_2Cl_2(H_2O)_2$ that appears to be a precursor for the formation of brookite.[126] Precipitation of $TiCl_4$ with ammonia and hydrothermal/solvothermal treatment at 250 °C leads to cubiclike anatase particles.[127] The presence of other acids can also influence the synthesis. Aruna et al.[109] reported the preparation of 20 nm rutile particles by hydrolysis of TTIP in HNO_3 solution at 250 °C in the absence of other compounds. These authors claim that vigorous stirring of the solution during hydrothermal treatment is fundamental for achieving the pure rutile phase. Under similar conditions, in the presence of ethanol, Chae et al.[6] prepared anatase nanocrystals where the particle size decreased by 5 times when the ethanol concentration was increased.

Anions can also dramatically influence the size, shape, and phase composition of titania prepared through hydrothermal methods. A comprehensive study looking at this effect was recently reported by Liu et al.[128] Anatase octahedral particles of about 20 nm in size were obtained by hydrothermal treatment of $Ti(OH)_4$ in a water/2-propanol mixture. Rutile rods (100–200 nm) were obtained when ammonium oxalate was added, while brookite particles (60–80 nm) were recovered when lactate salts were used. F^- anions caused the anatase particles to become truncated to expose larger {001} facets, while SO_4^{2-} and acetate anions led to the formation of rods. Interestingly, all three of the phases and the different shapes evolved from similar anatase seeds formed at early stages of the hydrothermal treatment, implying that the anions may bind to particular facets of the seeds and thus direct further growth. Gai et al.[129] conducted a similar study but started from several titanium precursors [$Ti(SO_4)_2$, titanium butoxide, $TiCl_4$, and TiF_4] in combination with hydrazine. In their case, $TiCl_4$ resulted in elongated structures (rods of up to 130 nm in length), whereas $Ti(SO_4)_2$ and TiF_4 produced bipyramidal anatase particles, and titanium butoxide led to irregular precipitates. Interestingly, SO_4^{2-} and F^- anions were found to preserve the pure anatase phase, while Cl^- and butoxide anions resulted in the formation of mixed phases. This fact was attributed by the authors to formation of an initial titanate precursor that was then dissolved under basic conditions to titanate octahedral units, which were reassembled to form the final products. The strength with which the anion binds the Ti^{4+} cations on the growing titanate surface then determines the formation of one morphology over another. Jiao et al.[130] also reported on the use of sodium phosphate (Na_3PO_4) as additive to produce octahedral crystals and hollow structures and proposed a shift of the valence and conduction band in these structures.

Small, uniform anatase nanocrystals were produced by hydrothermal treatment of titanium bis(ammoniumlactato) dihydroxide.[131] The particle size could be controlled between 2 and 5 nm by changing the reaction temperature in the range 120–300 °C. Lactic acid, produced by the hydrolysis of the titanium precursor, was suggested as being responsible for maintaining a small particle size by strongly adsorbing to the surface of the growing titania crystallites. The final particle size is directly linked to the temperature at which the reaction is conducted, suggesting a link to the thermodynamics of the Ti–

lactic acid bond on the surface of the crystals. In a similar procedure, the use of urea was shown to have a profound effect onto the obtained titania phase. Low concentrations of urea during hydrothermal treatment led Kandiel et al.[132] to obtain mainly small anatase nanoparticles, but at higher concentrations brookite rods were the main product. This effect can be related to the hydrolysis process that urea undergoes in aqueous solutions at temperatures above 90 °C. The slow release of OH^- during this process raises the pH and influences the way the titanium octahedral units arrange to form the final phase (see Introduction). By systematically varying the reaction conditions and isolating the products at different reaction times, the authors suggested that there was no phase transformation during the synthesis. Instead, direct formation of either anatase or brookite seeds under the specified conditions was responsible for obtaining anatase particles or brookite rods (Figure 9).
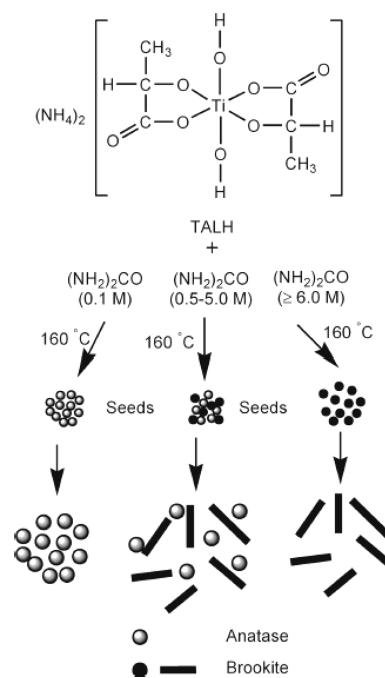

Figure 9. Suggested reaction pathways for the hydrolysis of titanium bis(ammoniumlactato) dihydroxide in the presence of varying concentrations of urea to form either anatase particles or brookite rods or mixtures thereof. Reprinted with permission from ref 132. Copyright 2010 American Chemical Society.

The most thermodynamically stable shape of anatase crystals is bipyramidal, due to the low energy of the {101} facets. HF was recently discovered to bind selectively to the {001} facets, preferentially exposing this facet in the resulting crystals. This effect was clearly demonstrated by Liu et al.,[133] who exploited the hydrolysis and hydrothermal treatment of titanium butoxide in water/H_2O_2 solution at different concentrations of HF. Small, spherical anatase nanoparticles were obtained when no HF was added to the solution; but at increasing amounts of HF, truncated structures exhibiting high percentages of {001} facets were observed with a roughly 100 nm edge length (Figure 10).

Hydrothermal synthesis in combination with HF was also used to prepare hollow microspheres formed by nanocrystals with mainly exposed {001} facets starting from titanium powder, HF, and H_2O_2 (Figure 11).[134]
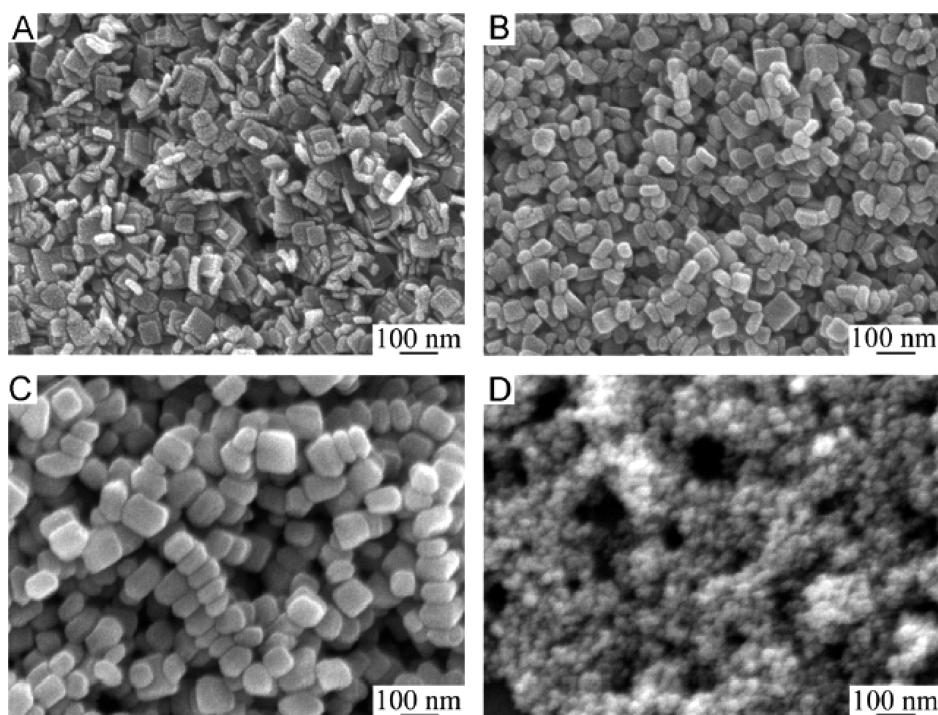
Figure 10. Scanning electron microscopy (SEM) images of TiO$_2$ nanostructures obtained by hydrothermal treatment of titanium butoxide with varying amounts of HF and H$_2$O$_2$ added: (A) 1 mL of HF; (B) 1.0 mL of HF and 6.0 mL of H$_2$O$_2$; (C) 0.5 mL of HF and 6.0 mL of H$_2$O$_2$; (D) 6.0 mL of H$_2$O$_2$. Reprinted with permission from ref 133. Copyright 2013 Elsevier.
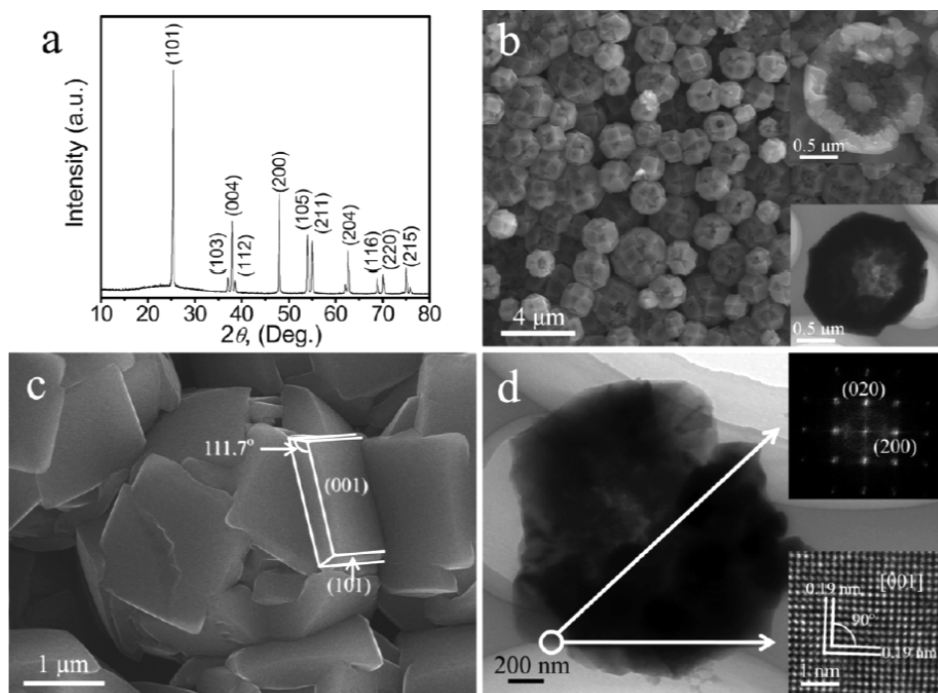
Figure 11. Hollow microspheres prepared by hydrothermal treatment and HF. (a) XRD pattern; (b) low-magnification SEM image, with a broken microsphere and TEM image in top and bottom insets; (c) SEM image showing the nanoplates forming the hollow structures; (d) TEM image of a single anatase plate with the HRTEM image (bottom inset) and the corresponding fast-Fourier transform (FFT) pattern (top inset). Reprinted with permission from ref 134. Copyright 2012 Elsevier.

Interestingly, these structures evolved during the synthesis, initially forming solid spheres with smooth surfaces and transforming to hollow, {001}-exposed samples after prolonged hydrothermal treatment, suggesting a redistribution of the titania crystals from the interior to the exterior of the structures, indicative of the Kirkendall effect. This effect might be driven by the presence of H$_2$O$_2$ in combination with F$^-$ (see below).

Similar structures were prepared from titanium powder and HF.[135] In this case, however, the structures were not hollow, demonstrating the important role of H$_2$O$_2$ in the above-

mentioned case to create the hollow structures. The growth of titania spheres in this case was found to start with flower-like str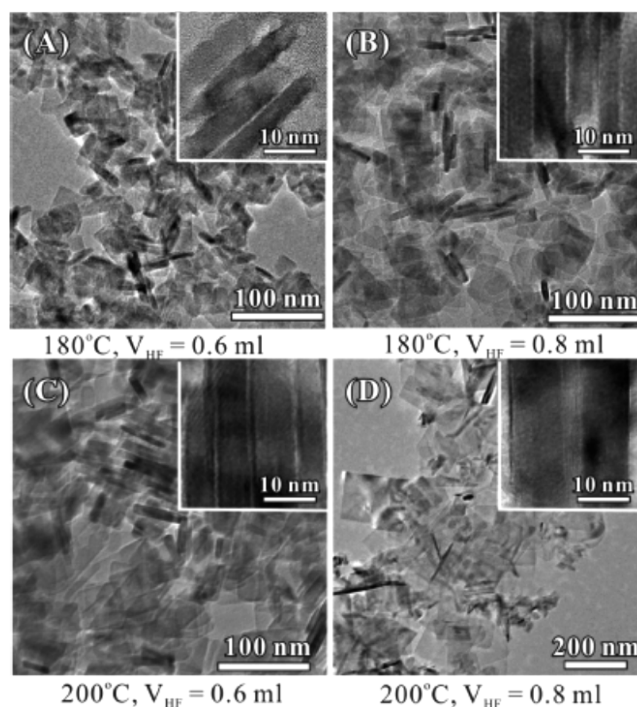uctures with exposed {101} facets. The slow hydrolysis of H_2TiF_6 then produced HF which promotes the faster growth of the {001} facets and almost completely replace the {101} facets by the end of the hydrothermal process (Figure 12).

Figure 13. TEM images of TiO_2 nanosheets synthesized at (A, B) 180 °C and (C, D) 200 °C with increasing amounts of hydrofluoric acid. A larger amount of HF results in larger nanocrystals. Reprinted with permission from ref 138. Copyright 2009 American Chemical Society.

Figure 12. Field emission (FE) SEM images of hierarchical nanospheres obtained at different reaction times: (a) 0, (b) 0.5, (c) 1, (d) 3, (e) 5, (f) 7, (g) 10, and (h) 15 h. (Insets) High-magnification SEM images. Also, schematic illustration of the formation of hierarchical titania spheres with exposed {001} facets is shown. Reproduced with permission from ref 135. Copyright 2012 Wiley–VCH.

Liu et al.[136] started from $Ti(SO_4)_2$ to prepare nanocrystalline anatase with exposed {001} facets. Nanoplates were prepared by starting from titanium isopropoxide.[137] Increasing the amount of HF usually grows larger {001} facets but with the result that nanocrystals also grow in size (Figure 13).[138]

In order to avoid the use of the very dangerous HF, Dai et al.[139] manipulated the structure of titania nanocrystals via a complex method beginning with formation of an amorphous titania species embedded within PVP fibers. The precursor is

formed by electrospinning titanium isopropoxide and PVP and treating the obtained nanocomposite precursor under hydrothermal conditions, with acetic acid used to control the pH. At the moderately acidic pH of 1.6, bipyramidal nanocrystals form with a main axis of about 20 nm. The amount of exposed {001} facets, however, is quite low (less than 10%). The authors claim that the electrospinning process was essential to obtain nanocrystals with uniform shapes. At pH lower than 1.6, the growth of {001} facets was suppressed, while at higher pH, oriented attachment favored elimination of the high-energy facet. These authors explain the results by suggesting that the PVP molecules may bind preferentially to the {001} facets within a specific pH window around 1.6. Additionally, presence of the acetate ion was also found to be crucial for obtaining the morphology, as other inorganic acids such as nitric, sulfuric, or hydrochloric acid produced large aggregates. In another attempt to step away from HF, Ma et al.[140] started with TiF_4 and obtained microparticles in which nanosheets possessing {001} facets extended outward from the surface. Most likely, TiF_4 decomposition evolved HF or F^- in situ, which controlled the shape of the titania crystallites.

An interesting variation of the hydrothermal treatment utilizes supercritical fluids as solvents. These types of solvents are attractive because they have characteristics that are typical of gases (diffusivity, viscosity etc.) but solvation capabilities and densities that are typical of liquids. Supercritical CO_2, in particular, has received attention recently as a green solvent. Wang et al.[141] used it in combination with ethanol and water under hydrothermal-like conditions (120 °C, 150 bar) to obtain well-crystallized anatase nanocrystals about 5 nm in size.

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dx.doi.org/10.1021/cr500170p | Chem. Rev. 2014, 114, 9319–9345
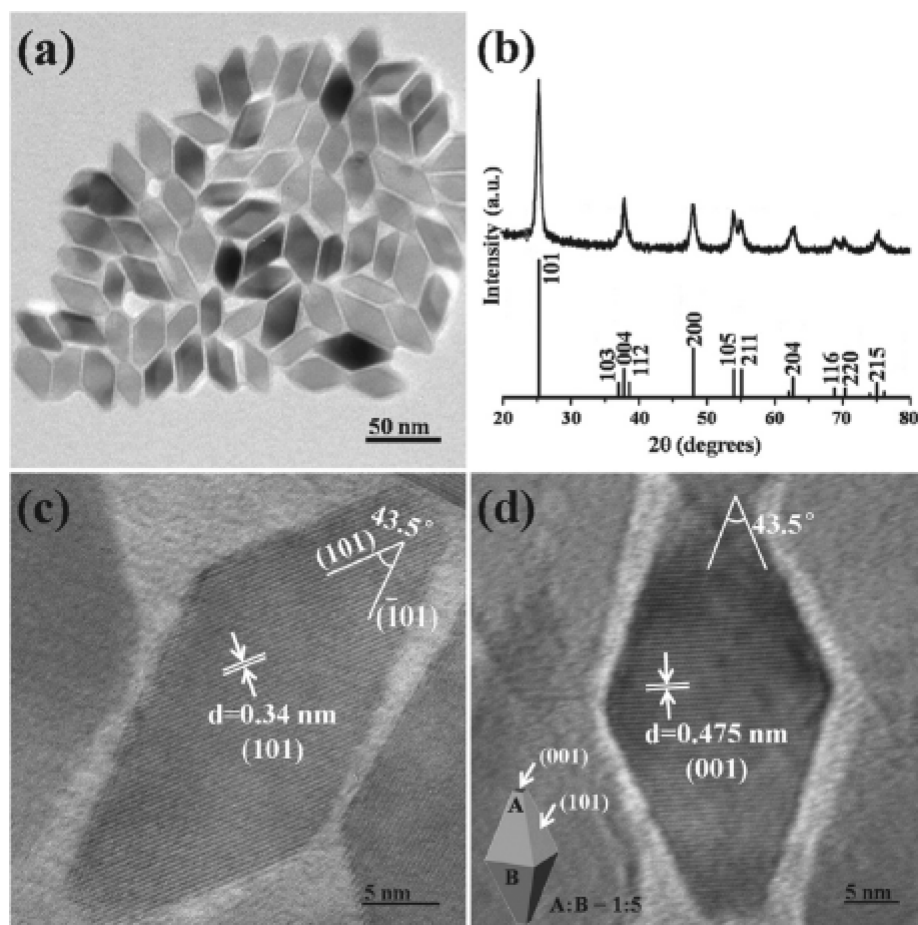
Figure 14. (a) TEM image of anatase TiO$_2$ nanobipyramids prepared under solvothermal conditions at 250 °C for 24 h with a molar ratio of titanium butoxide to NaF of 5:2. (b) XRD pattern of the as-prepared TiO$_2$ nanobipyramids. (c, d) HRTEM images of nanobipyramids. (Inset) Schematic model of a typical nanobipyramid. Reprinted with permission from ref 151. Copyright 2011 American Chemical Society.

5. NONAQUEOUS METHODS

In nonaqueous methods, water is not used as the primary reaction solvent, such that titania can form through mechanisms other than hydrolysis and condensation. The terms nonaqueous sol−gel and nonhydrolytic sol−gel were coined early on and continue to be used to describe the synthesis of oxide nanocrystals when water is not included as a reactant, although they are not always well-distinguished in the literature. Nonhydrolytic sol−gel describes reactions in which an oxide forms without any involvement from water, through reactions with oxygen-containing organic molecules, while in nonaqueous sol−gel processes, hydrolysis occurs through reactions with water produced in situ.[142] The term "sol method" has also been applied to this class of reactions, although the origin of this term is not entirely clear.[1] Commonly observed mechanisms for titania formation under these conditions include the following (see also section 3):[51,143] (1) alkyl halide or ether elimination by cross-reactions between different titanium precursors to form Ti−O−Ti and elimination of the remaining precursor structure, such as between titanium halides and titanium alkoxides; (2) thermal decomposition of oxygen-containing precursors in which the oxygen atom is incorporated in the final product and there is elimination of an unsaturated organic compound (such as alkene) from the remaining part of the precursor structure; and (3) reactions that form water (or another activated form of water) in situ,

such as esterification or aminolysis by reaction of a metal carboxylate precursor with an alcohol[144] or an amine.[145]

It is important to note that, without careful study, it is often unclear whether water is produced during a given reaction, so the terms nonaqueous sol−gel and nonhydrolytic sol−gel are often used interchangeably. One proposed advantage of the nonaqueous approaches is better control over reaction rates than is possible in sol−gel chemistry, where hydrolysis typically occurs very quickly and is difficult to modulate.[146] When water is not present or produced in situ, hydrolysis and condensation can generally be better controlled because these reactions occur much more slowly. Additionally, the inclusion of surfactants and organic ligands (which are sparingly soluble in aqueous-based mixtures) has provided additional tools to tune the reactivity of the precursors resulting in unprecedented control over the morphology of titania nanocrystals. For the purposes of this review, we separate nonaqueous synthetic approaches into two categories: (1) solvothermal, which are those conducted in an autoclave with nonaqueous primary solvents at elevated pressures, similar to hydrothermal methods, and (2) nonaqueous surfactant-assisted, which are conducted at or near atmospheric pressure by conventional air-free Schlenk line techniques.

5.1. Solvothermal Methods

Solvothermal methods are very similar to hydrothermal except that the primary solvent used is not water, although water is
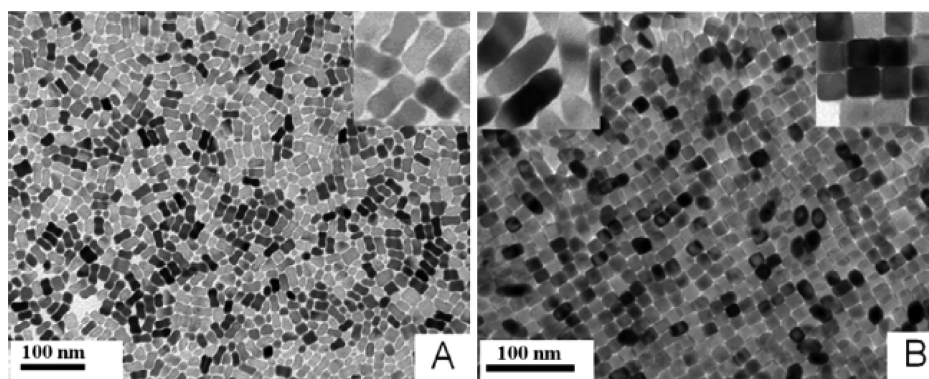
Figure 15. TEM images of (A) dog-bone-shaped TiO₂ and (B) truncated and elongated rhombic TiO₂. (Insets) High-magnification images of the corresponding shapes (left, longitudinal view; right, cross view of panel B). Reprinted with permission from ref 154. Copyright 2009 American Chemical Society.

sometimes added to induce hydrolysis. In contrast to hydrothermal, a larger variety of surfactants or structure-directing agents can be employed in solvothermal methods to drive the shape and morphology of the crystallites. The choice of the solvent has also been found to dramatically influence the shape and size of the formed crystallites. For example, Du et al.[147] showed that octahedral titania particles could be obtained in toluene whereas spheres were obtained in ethanol following a solvothermal treatment of titanium butoxide in the presence of CTAB.

Under solvothermal conditions, titania formation can occur even in the absence of any additional compounds other than an oxygenated titanium precursor such as a titanium alkoxide.[148] This is because some titanium alkoxides can thermally decompose into titania and an unsaturated (alkene) organic compound. Indeed, Kominami et al.[149] demonstrated that titanium *tert*-butoxide can decompose into titania micro-particles (composed of smaller titania nanocrystals) at high temperature (200−300 °C) in organic solvents but that primary and secondary titanium alkoxides cannot, even at temperatures as high as 300 °C. This fact can be related to both the strength of the C−O bond in the alkoxide, which must be broken to form the required Ti−O−Ti bonds, and the ease with which the alkyl group can undergo elimination to produce the unsaturated alkene.

An additional benefit of the solvothermal versus the hydrothermal process is that organic surfactants can be employed, which solubilize the nanocrystals in nonpolar solvents through the formation of inverse micelles. Kim et al.[150] used oleic acid to decompose TTIP at 250 °C in toluene, resulting in ∼6 nm crystallites that became elongated upon concentration of the reaction or increased oleic acid concentration.

Surfactants, in combination with other additives, can also help control the formation of specific facets in titania. For instance, Chen et al.[151] used oleic acid in combination with NaF to drive the formation of specific shapes based on the truncated bipyramidal geometry. In their preparation, these authors started from titanium butoxide, oleic acid, NaF, and water and performed a solvothermal treatment at 250 °C for 24 h. The resulting product was composed of anatase particles of about 40 nm in length (main axis) with a rhombic projection consistent with a truncated tetragonal bipyramidal geometry (Figure 14).

The authors found that the main mechanism for the formation of the particles was Ostwald ripening, with bimodal size distributions of particles observed at intermediate reaction stages. It is interesting to note that despite the use of F⁻ ions during the synthesis, large percentages of {001} facets were not produced in the final crystals, although some truncation of the basic structure was observed at lower titanium butoxide/NaF ratios. The authors claimed that the primary role of NaF was in the formation of faceted bipyramidal nanocrystals, as the use of NaCl, NaBr, or sodium oleate resulted in more spherical particles. Similar observations were also reported by Zhu et al.,[152] which, despite the use of TiF₄ in combination with TiCl₃, did not result in the observation of {001} facets. Instead, the solvothermal treatment of the two precursors in ethanol provided 15 nm anatase nanocrystals enclosed by {101} facets with a characteristic blue coloration induced by the presence of Ti³⁺ in the structure, as previously reported in other preparations.[153] The authors of the study propose that the sample exhibits a special configuration in which a reduced titania core (TiO₂₋ₓ) embedded inside a fully oxidized titania shell, as suggested by Raman, which indicates a slight shift and peak broadening of the Eg mode.

Outstanding control over the morphology of titania was demonstrated by Dinh et al.,[154] utilizing an ethanol-based solvothermal process in the presence of steam. The authors showed that highly crystalline particles of pure anatase were prepared in a variety of shapes by carefully tuning the amount of oleylamine and oleic acid added to a solution of titanium butoxide during solvothermal treatment at 180 °C. For example, by changing the titanium/oleic acid/oleylamine ratio from 2/6/4 to 2/5/5, these authors were able to produce either dog-bone-shaped or truncated rhombic crystals, respectively (Figure 15). The authors rationalized the shape control on the basis of their ability to finely control hydrolytic and nonhydrolytic rates under the reaction conditions. Titanium oxyhydroxide will initially form through the reaction of titanium butoxide with water (steam) present in the reaction mixture. However, complexation by oleic acid could hinder further hydrolytic condensation of this species, favoring instead a nonhydrolytic pathway operative when oleylamine is present that cleaves the titanium carboxyhydroxide bond to produce crystalline titania through aminolysis. Tuning of the specific exposed facets was realized by tuning of the oleic acid/oleylamine ratio, by changing the concentration of the titanium precursor, or by altering the temperature of the reaction,
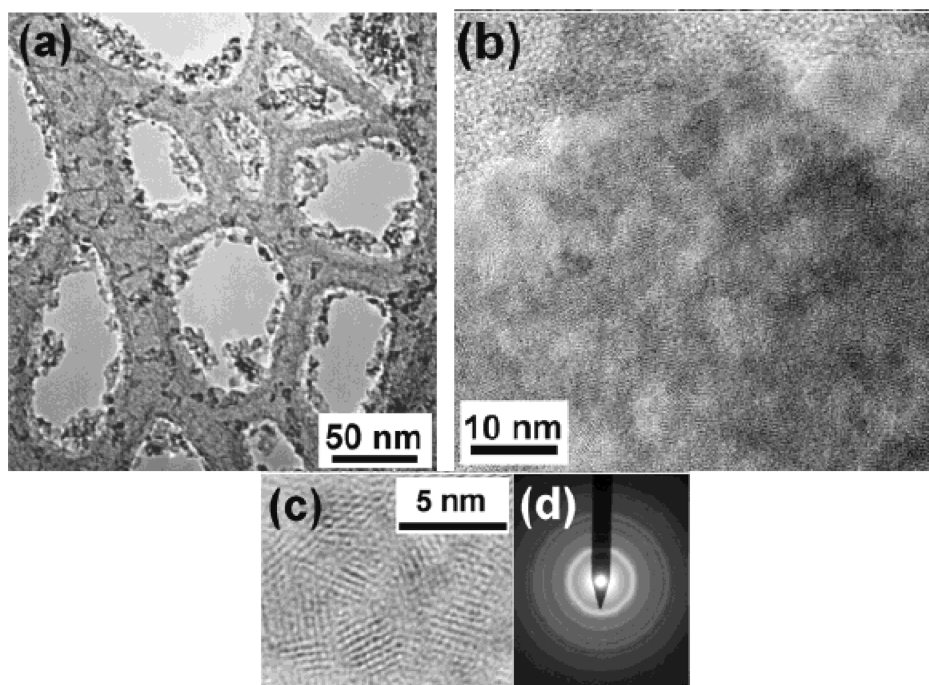
Figure 16. Representative TEM micrographs of as-synthesized anatase nanoparticles, obtained at 40 °C via the "benzyl alcohol" route. (a) Overview; (b) higher magnification illustrating the crystallinity of the particles; (c) lattice fringes of single particles with an average diameter of about 4 nm; (d) selected area electron diffraction rings. Reprinted with permission from ref 163. Copyright 2002 American Chemical Society.

allowing for a rich mixture of shapes including also bars, dots, and rods to be obtained.

Similarly to hydrothermal processes, the use of $TiCl_4$ as precursor can lead to formation of rutile particles instead of the commonly observed anatase. Roca and Leite[155] found that higher concentration of $TiCl_4$ and a less polar solvent such as 1-octanol compared to terathane-1000 (a glycol) favored the rutile phase because of the retention of HCl on the surface of the growing titania particles. The use of HF as structure-directing agent is also prevalent in solvothermal syntheses in which water is present in the solvent mixture. Micrometer-size sheets were prepared from TiF_4 by use of 2-propanol as the primary solvent.[156]

In a similar approach, the ionic liquid [bmim][BF_4] has been utilized in the solvothermal synthesis of titania as both a fluoride source and a ligand, allowing for production of anatase titania cuboids of variable aspect ratio and edge lengths in the 60−830 nm range, enclosed by higher energy {100} and {001} facets.[157] Several elements dictated the final morphology that the authors were able to produce: modification of the reactivity of titanium tetraisopropoxide by complexation with acetic acid, amount of ionic liquid, and amount of water. Interestingly, smaller crystals were obtained upon decreasing the amount of acetic acid in the mixture, suggesting that the nucleation rate was slower when the titanium precursor was protected by a larger amount of acetic acid. The BF_4^- anion served as the fluorine source, able to stabilize {001} facets thanks to its decomposition under synthesis conditions in the presence of trace water. The organic part of the ionic liquid ([bmim]$^+$) was also shown to provide stabilization of the {100} facets that were then exposed in the final crystals. Interestingly, the cuboids showed a resistance toward the anatase-to-rutile phase transformation up to 800 °C, probably due to a combination of kinetic limitations due to the large size and to the nature of the exposed facets. In a different solvothermal synthesis

involving acetic acid, anatase wires were prepared by use of N,N-dimethylformamide (DMF)/acetic acid as solvent mixture and lithium acetate as modifier.[158] The nanowires grow along the [101] direction to yield structures of hundreds of nanometers in length and 5−20 nm in diameter. Similarly, small anatase nanocrystals that are soluble in a range of solvents were prepared by solvothermal synthesis in trifluoroacetic acid from amorphous titania powder as the precursor.[159]

With ethylene glycol as solvent, pure brookite particles were reported from $TiO(acac)_2$ as the precursor in a solvohydro-thermal procedure at 300 °C.[160] Important in this case was the addition of sodium laurate as a Na^+ source, which led to formation of the brookite phase.

In a combined hydro/solvothermal method, Li and co-workers[161] described the use of linoleic acid as surfactant for the preparation of a variety of materials in nanocrystal form. This method was then applied to prepare small anatase nanocrystals and nanorods but in cyclohexane.[162] These authors were able to tune the length of the rods and the size of the particles by changing the amount of linoleic acid and NH_4HCO_3, used to generate water in situ, driving the formation of Ti−O−Ti bonds.

The "benzyl alcohol" route, developed by Niederberger et al.,[163,164] is another versatile method to prepare titania and other oxides. It consists of the reaction between $TiCl_4$ and benzyl alcohol to form an intermediate alkoxide that is then hydrolyzed to form the final titania crystallites. Benzyl alcohol serves also as the reaction medium, therefore the distinction between solvothermal and nonaqueous surfactant-assisted for this method is not very clear. The method results in formation of titania nanoparticles at very low temperatures (<100 °C and as low as 40 °C, Figure 16) with sizes tunable in the 4−14 nm range depending on the aging time, temperature, and benzyl alcohol/$TiCl_4$ ratio. Although the particles are colloidally stable as synthesized, they tend to be insoluble after washing and

drying. The addition of surfactants such as trioctylphospine was found to improve the solubility and solution stability of the washed particles. The solubility of the particles can be further tailored in water or organic solvents by using dopamine or 4-*tert*-butylcatechol, respectively, during the synthesis.[165]

Polymer melts can also be used as solvents for solvothermal preparation of TiO_2 crystallites. Poly(1,4-butanediol), for example, was employed as a solvent and reaction medium.[166] The ether moieties in the polymer can react with $TiCl_4$ to eliminate organic halide and HCl, forming 8 nm TiO_2 particles at temperatures as low as 120 °C that are soluble in common organic solvents such as ethanol, tetrahydrofuran, or DMF (Figure 17).
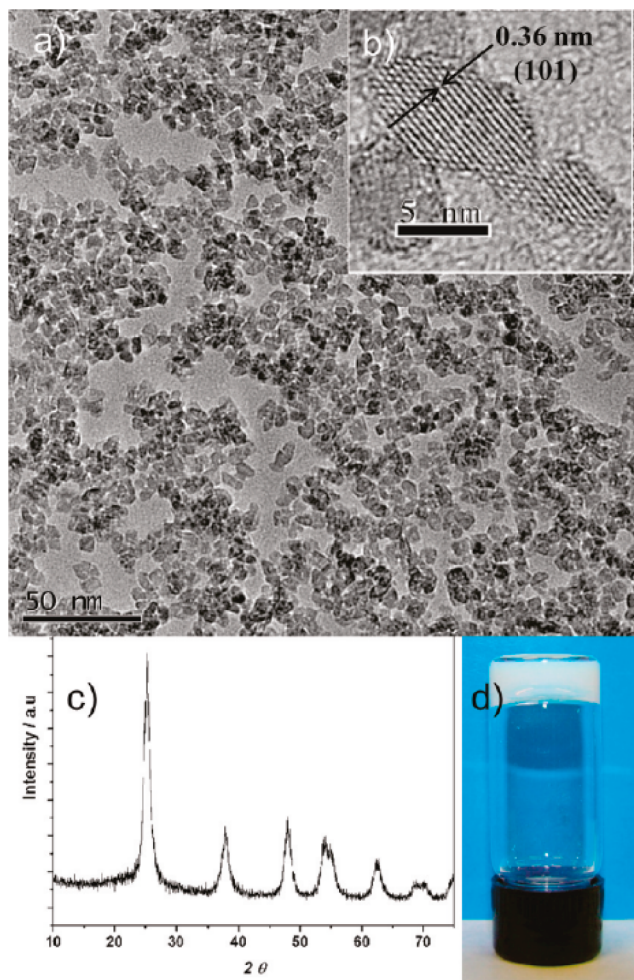
Figure 17. (a) TEM and (b) HRTEM images of TiO_2 nanoparticles prepared in molten poly(1,4-butanediol) and $TiCl_4$. (c) XRD pattern of 8 nm anatase nanocrystals. (d) DMF solution at high concentration of TiO_2 particles; the particles show thixotropic properties. Reprinted with permission from ref 166. Copyright 2010 American Chemical Society.

5.2. Nonhydrolytic Methods

Nonhydrolytic surfactant-assisted processes are based on reactions that produce the required Ti—O—Ti bonds in the presence of surfactants that modulate the growth of titania, while typically also participating in the formation mechanism. This chemistry has evolved from methods developed for the synthesis of colloidal quantum dots and other materials, which have revolutionized the synthesis of size- and shape-controlled

nanocrystals. Such methods have been utilized to produce a variety of metal oxide systems including tin oxide, tungsten oxide, iron oxide, and zinc oxide, as well as titania. One of the advantages of nonaqueous surfactant-assisted synthesis is that the reactivity of the titanium precursors can be further modulated by the choice of the surfactant molecules that act as protecting agents.

Colvin and co-workers[167] were among the first to exploit the reaction between titanium halides and titanium alkoxides or with ethers (see also section 3) to produce colloidally stable titania particles via a nonhydrolytic approach. The reaction proceeded to completion, resulting in nanoparticles that were soluble in organic solvents due to the presence of trioctylphosphine oxide (TOPO) capping ligands. Alkoxides or ethers with branched alkyl groups (e.g., *tert*-butyl) were found to increase the reaction rate, while the choice of titanium halide was found to alter the particle size, with the largest anion, iodide (I^-), producing the smallest particles, followed by bromide, chloride, and fluoride with increasing particle size. These observations are in accordance with an S_N1-type mechanism in which a carbocation is formed from the alkoxide, which then reacts with the halide from the titanium halide precursor. A similar method was also employed to prepare 2.5 nm amorphous titania particles that were then used as precursor for the synthesis of rods through oriented attachment.[168] TOPO was again used as the solvent and stabilizing agent for producing 3−5 nm titania crystals from thermal decomposition of a modified alkoxide precursor.[169] In this latter case, it is likely that the alkoxide ligands act as the oxygen source that is incorporated in the final TiO_2 lattice. Yin and co-workers[170] used this method to prepare similarly small (5 nm) nanocrystals starting from titanium butoxide and $TiCl_4$ with TOPO acting as the solvent and ligand. The small crystals were then self-assembled into large, submicrometer-size spherical mesoporous particles.

The impact of surfactant binding during the growth of 0D and one-dimensional (1D) structures was studied by Cozzoli et al.[171] Pure anatase rods were obtained by hydrolysis of titanium isopropoxide solutions in pure oleic acid at temperatures in the range 80−100 °C in the presence of a base as a catalyst for Ti—O—Ti bond formation. Slow, in situ release of water by an esterification reaction in the presence of ethylene glycol resulted in spherical and nonuniform particles. Quick hydrolysis after the fast injection of water provided anisotropic growth. The authors hypothesized that the difference in reactivity was due to the existence of different precursors in solution under the two hydrolysis conditions. With a fast water injection, the system was kinetically driven to grow anisotropically because of a face-dependent surface density of −OX groups in the titania precursor and a directional reaction between polynuclear monomers in solution as dictated by the long oleic acid alkyl chains on the surface of the small nuclei (Figure 18).

Similar considerations were reported by Zhang et al.[172] during the preparation of 2.3 nm anatase particles and ultrathin nanorods by aminolysis of a titanium alkoxide/oleate precursor in organic solvent. When TTIP was reacted with oleic acid at high temperature in organic solvent, nanorods of tunable length were obtained by varying the concentration of oleylamine that was injected at high temperature. Again, as in the previous case, the coverage of specific facets by oleic acid was found to lead to the anisotropic growth of rods. Other syntheses with the combination of oleic acid and oleylamine were also reported to produce anatase rods under similar conditions.[173,174]
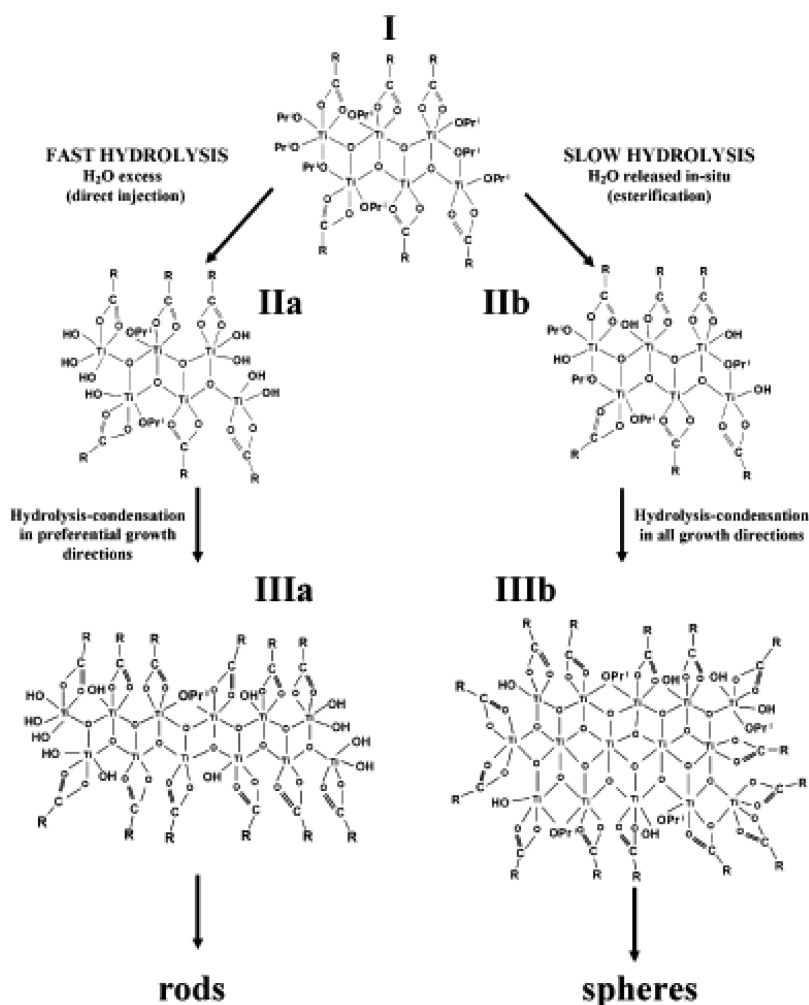
Figure 18. Hypothesized mechanism for anisotropic (route a) and isotropic (route b) growth of titania nanocrystals in oleic acid as pure solvent [-OPr^i = −CH(CH$_3$)$_2$ and R = oleic acid alkyl chain]. Reprinted with permission from ref 171. Copyright 2003 American Chemical Society.
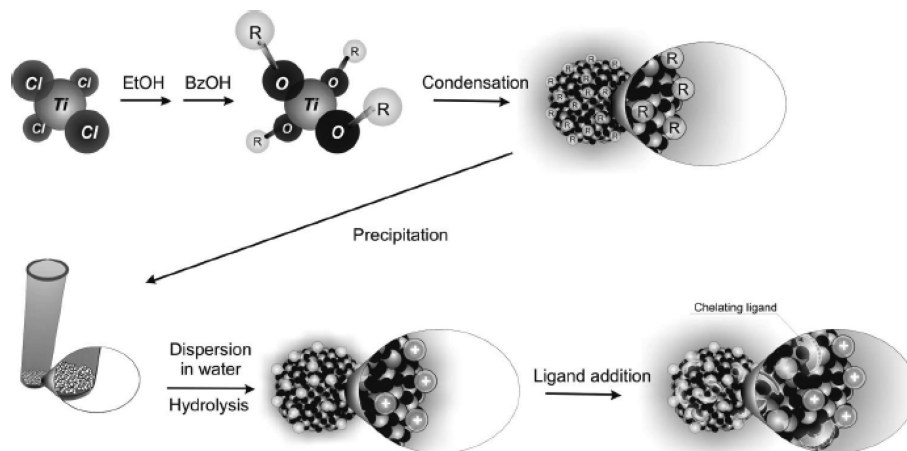
Figure 19. Synthesis of TiO$_2$ anatase nanoparticles by reaction of titanium ethoxide and TiCl$_4$, followed by treatment in benzyl alcohol and eventual ligand exchange. Reprinted with permission from ref 175. Copyright 2008 American Chemical Society.

Building on the basis of the "benzyl alcohol" route (see section 5.1), Kotsokechagia et al.[175] reported a modified strategy that combined a first nonaqueous phase, to better control size, phase, and crystallinity of the particles, with a water-based procedure, where surface groups are removed to yield "naked" or "ligand-free" nanoparticles (Figure 19).

The method exploited the reaction between TiCl$_4$ and ethanol in benzyl alcohol to produce 8−9 nm anatase particles. The authors claim that this initial reaction produces particles with ethoxy groups still on the surface because of the lower steric hindrance of the ethoxy group compared to the benzyl residue. The ethoxy groups can be then easily removed by

dialysis at low pH to provide the final "ligand-free" particles. After 9 h of reaction, anatase particles are formed with a primary size of 2−5 nm that agglomerated into secondary particles with a size of about 30 nm, as measured by light scattering (Figure 20).
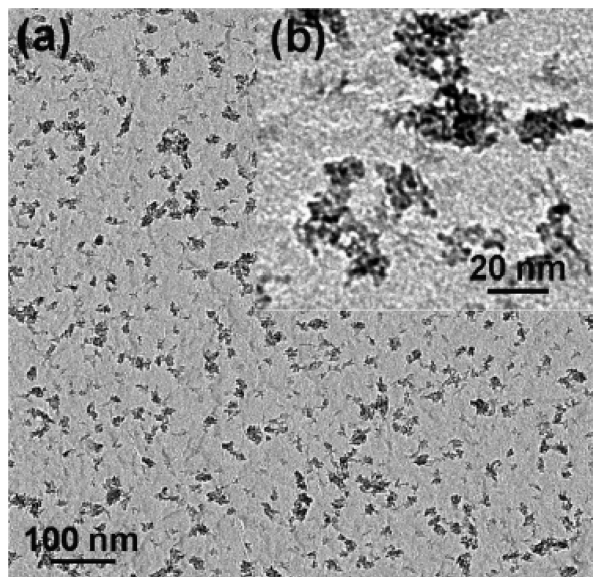
Figure 20. TEM images of anatase particles prepared by a combined nonaqueous/aqueous route: (a) low and (b) higher resolution images. Reprinted with permission from ref 175. Copyright 2008 American Chemical Society.

The anatase particles can then be successfully redispersed in water and functionalized with several ligands.[176] In a further study, these authors addressed the role of water in the growth of particles,[177] because the "benzyl alcohol" procedure is usually conducted under air, where trace amounts of water can be present. They found that water accelerated the kinetics for formation of titania particles and that more hydrophobic alkoxide ligands (such as isopropoxide group) allowed for better dispersion of the particles in water due to the lower agglomeration.

Wu et al.[178] also used benzyl alcohol as reaction medium, but in the presence of amines as ligands, to prepare titania sheets and rhombic anatase nanocrystals under solvothermal conditions. These authors found that the addition of small amounts of water and control of the reaction temperature allowed for the particles to transform from sheetlike to rhombic structures exhibiting high-energy {010} facets in a high ratio (43%). An attractive feature of this procedure is that the final crystals, capped by oleylamine, can be readily transferred into water by treatment with tetrabutylammonium hydroxide in ethanol. In another similar approach, a thiobenzoate titanium complex was used as precursor to form 6 nm anatase particles in benzyl alcohol under microwave irradiation.[179]

Similar to the benzyl alcohol route, Szeifert et al.[180] used *tert*-butanol as reaction medium in combination with microwave heating. At temperatures as low as 80 °C, small, crystalline anatase nanocrystals (3−4 nm) were formed. The possible mechanism involves a nucleophilic substitution of the OH^- ion derived from decomposition of *tert*-butanol to $TiCl_4$ and subsequent reactions to produce the final titania particles.

An "unconventional" organometallic method was developed by Tang et al.,[181] who reacted bis(cyclooctatetraene)titanium with dimethyl sulfoxide (DMSO) (eq 6) at room temperature to form titania.

$$Ti(COT)_2 + 2OS(CH_3)_2 \rightarrow TiO_2 + 2S(CH_3)_2 + 2COT \tag{6}$$
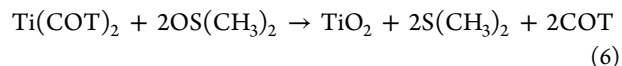
The very high reactivity of the titanium precursor was balanced by the less reactive DMSO to provide ∼5 nm nanocrystals that, when obtained in the presence of phosphine as ligand, were crystalline and colloidally stable (Figure 21). The nanocrystals were composed of brookite as the main phase. Particles of larger size (15 nm) and narrower size distribution can be obtained by reacting the two compounds at 120 °C.

The reaction between amines or alcohols and titanium−carboxylate complexes is another popular way to prepare titania nanocrystals via nonhydrolytic surfactant-assisted methods. The injection of one of the precursors into a hot solution containing the others is a viable way to induce burst nucleation and prepare uniform nanocrystals. A preliminary investigation in this area was reported by O'Brien et al.,[182] who mainly studied the preparation of $BaTiO_3$ nanocrystals via hot injection. These authors stated that by injecting TTIP into a solution of oleic acid in diphenyl ether followed by H_2O_2 solution to improve crystallinity, 10 nm titania nanocrystals could have been prepared. At this final point, inverse micelles were formed in which the further hydrolysis and crystallization of titania particles took place.

The good control that nonhydrolytic methods show in the hydrolysis and condensation rates to form the titania network can be advantageously used to prepare larger structures from smaller building blocks by addition of more precursors in solution. This method is usually termed seed-mediated synthesis, with the seeds being the small structures that are grown into larger ones by epitaxial growth in solution. A very elegant example of the use of this method in the preparation of titania structures was recently reported by Buonsanti et al.[183] These authors not only demonstrated fine control over the architecture by realizing 1D growth of titania into rods but also observed a phase transition from the original anatase seeds to the pure phase brookite rods. The reactions were based on the aminolysis of a mixed titanium chlorocarboxylate complex to form the seeds, followed by slow addition of titanium precursors, resulting in the unidirectional growth of brookite rods with controlled size. The same method was later applied to the preparation of branched titania structures by increasing the ratio of oleic acid to oleylamine during the reaction, demonstrating further control over the growth of titania in solution.[184] Building on this basis, Gordon et al.[153] demonstrated an impressive control over the structure, phase, and electronic properties of small anatase crystallites by manipulation of the precursors in solution under high-temperature, nonhydrolytic conditions (Figure 22). These authors found that the morphology of titania nanocrystals could be sensitively manipulated depending only on the choice of TiX_4 precursor (TiF_4, $TiCl_4$, or a 1:1 mixture) and the cosurfactants that initiate the precursor decomposition (1-octadecanol and oleylamine). As aforementioned, the presence of HF during hydrothermal syntheses of titania has been shown preferentially expose the {001} facet of anatase. In this work, HF was released in situ during the nonhydrolytic decomposition of a mixed titanium fluoride carboxylate complex, which resulted in the preferential exposure of the {001} facet.
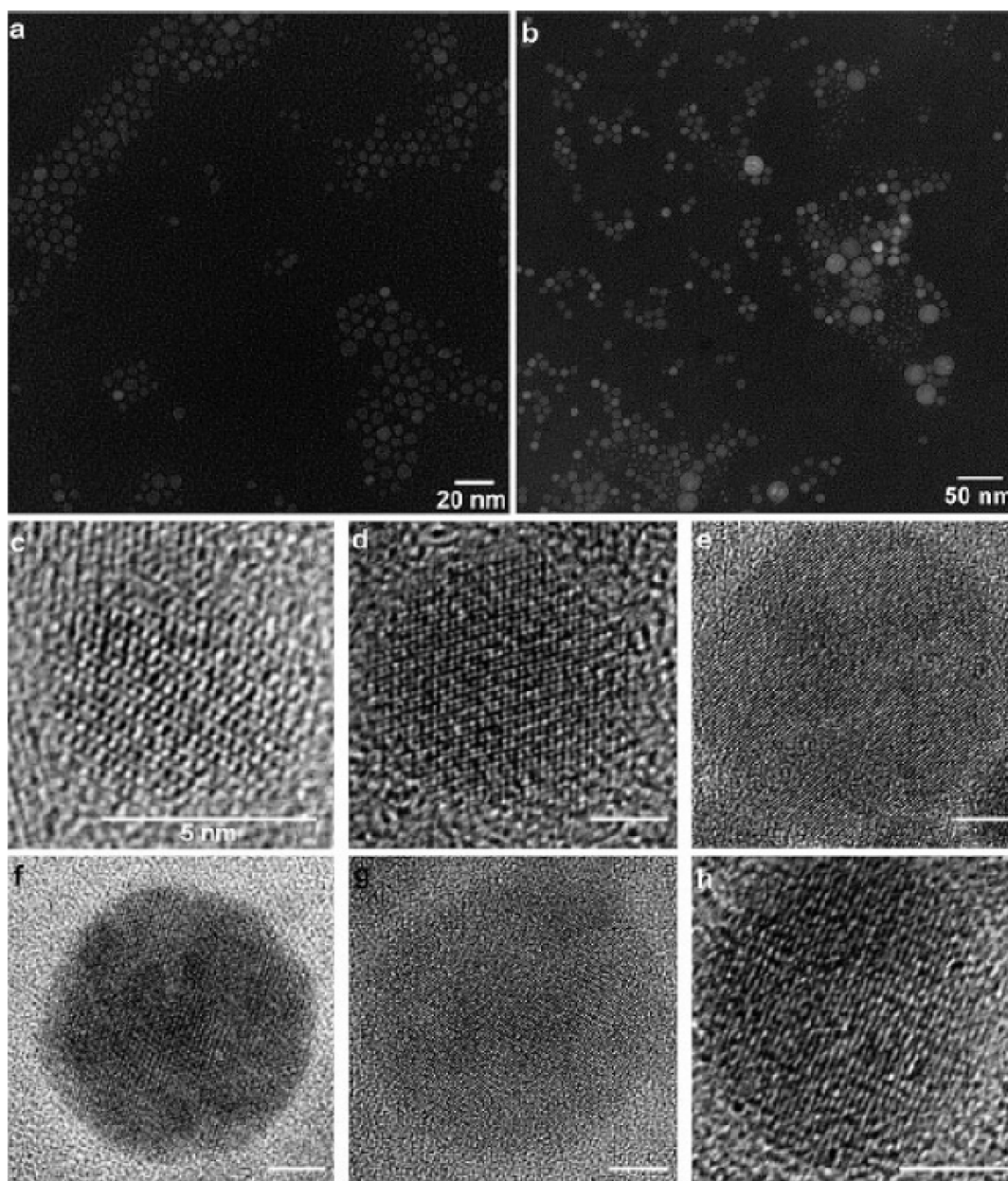
Figure 21. A selection of TEM and HRTEM images of anatase nanocrystals obtained from the reaction between Ti(COT)$_2$ and DMSO at room temperature with tributylphosphine oxide/tributylphosphine as surfactants. (a) Particles redispersed in CHCl$_3$ after being precipitated from the reaction solution by hexane. (b) Particles from the supernatant. (c–g) High-resolution TEM images of the particles: (c, d) particles from sample a, which are single-crystalline; (e–h) large particles from sample b. High-resolution TEM analysis reveals the various internal structures of these particles: (e) hollow particle, (f) polycrystalline particle that contains different domains, and (g, h) single-crystalline. The scale bars in images c–h all correspond to 5 nm. Reprinted with permission from ref 181. Copyright 2005 American Chemical Society.

By mixing two titanium halides in a 1:1 ratio, nanocrystals with an intermediate level of {001} facet were produced. In addition, the choice of cosurfactant was shown to have a dramatic effect on the proportion of {001} facet exposed, with 1-octadecanol resulting in significantly more {001} facet than oleylamine. This is rationalized on the basis of the ability of oleylamine to react with HF, forming a primary ammonium fluoride salt, effectively sequestering HF from the reaction and inhibiting exposure of the {001} facet.

In another example of the use of ionic liquids as both solvent and surfactant in the synthesis of titania nanocrystals, Ding et al.[185] used microwave irradiation to prepare highly truncated, cubiclike titania nanocrystals of about 9 nm in size. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]$^+$[BF$_4$]$^-$) was found to react with TTIP to form a partially hydrolyzed polyanion as an intermediate, which then decomposed into the final anatase nanocrystals.

6. TEMPLATED APPROACHES

In previous sections, synthetic approaches have been described in which the morphology of nanosized titania is altered through reaction conditions, such as reactant concentrations, temperature, and the presence of structure-directing agents. An alternative approach is to utilize templates to program the morphology of titania nanoparticles. In general, template approaches can be organized into two broad categories, soft
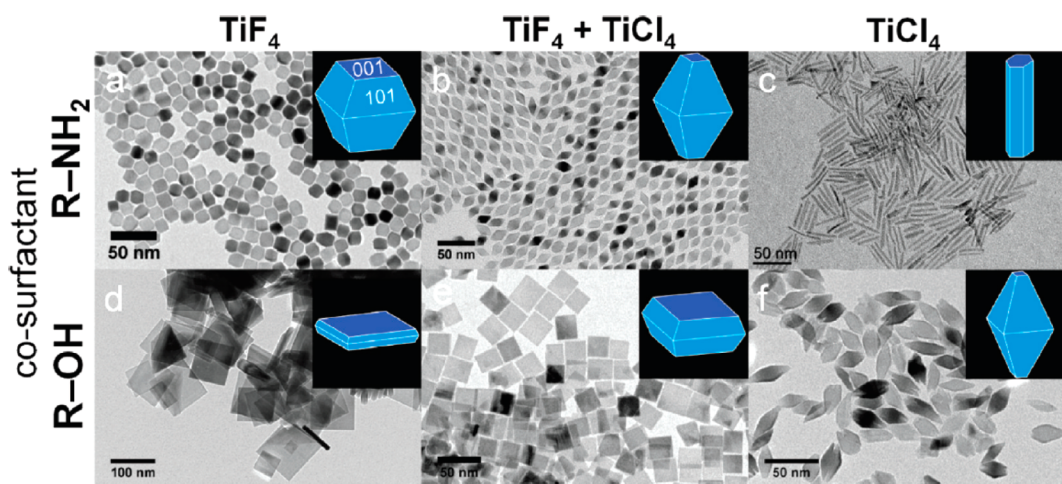
Figure 22. TEM images of TiO$_2$ nanocrystals synthesized from either (a, d) TiF$_4$, (b, e) a mixture of TiF$_4$ and TiCl$_4$, or (c, f) TiCl$_4$. Nanocrystals depicted in panels a−c and d−f are synthesized in the presence of oleylamine and 1-octadecanol, respectively. Reprinted with permission from ref 153. Copyright 2012 American Chemical Society.

and hard. Soft templates are formed from flexible organic or biologically based molecules, such as microemulsions, micelles, or proteins, whereas hard templates are rigid structures such as inorganic colloids or polymer beads. If conditions are found in which titania can be seeded inside or on top of a template, this represents a very powerful means to control particle morphology.

6.1. Soft Templates

Soft templating approaches have been used for many years in the synthesis of titania nanocrystals and can be broken down into two main categories, microemulsion or micelle-based and biological. Microemulsions are thermodynamically stable dispersions in which amphiphilic surfactants (and very often cosurfactants) stabilize small droplets of one liquid within a second liquid with which it is immiscible. Microemulsions are often defined as either oil-in-water or water-in-oil (reverse), although supercritical CO$_2$ may also be used as solvent. Similar to microemulsions, micelles are aggregates of surfactants that form in solution when the concentration of surfactant exceeds the critical micelle concentration (cmc). In aqueous solutions, the nonpolar tails of the surfactant cluster in the interior of the micelle and the polar head groups protrude outward (a normal micelle), while in a nonpolar phase, the polar head groups are in the interior and the nonpolar tails extend outward (a reverse micelle). The typical shape of a micelle is spherical, although it can be tuned depending on surfactant type and concentration.[186] Micelles can be filled with liquid of appropriate polarity to form swollen micelles, which are nearly indistinguishable from microemulsions. For this reason, the terms micelle and microemulsion are often used interchangeably.

In both microemulsions and micelles, the droplets that are stabilized by the surfactants may act as nanoscale reactors in which precursors are dissolved and react to produce nanoparticles of a variety of materials.[187,188] In the case of titania, alkoxides that are soluble in hydrocarbons are very useful precursors and can be used in reverse microemulsions or swollen reverse micelles. Their hydrolysis inside the water droplets can produce nanoscale particles that are stabilized by the surfactants. The powders obtained in this way are usually amorphous because the process is conducted at room temperature and must be thermally treated to convert into TiO$_2$.[189] Kim et al.[190] studied how the water-to-surfactant ratio,

water-to-titanium alkoxide ratio, temperature, feed rate, and ammonia concentration influenced the properties of titania particles prepared in a microemulsion approach. Several groups have also reported the precipitation of Ti(OH)$_4$ by combining a microemulsion containing TiCl$_4$ in water droplets with another containing ammonium hydroxide.[189,191] Upon mixing, the two microemulsions merged, resulting in precipitation that was confined within the droplets stabilized by surfactants. Particles were tunable in the small size range, as dictated by the microemulsion composition (water/surfactant ratio in particular). In a unique approach, amorphous titania nanoparticles have also been formed in hydrated reverse micelles dispersed in liquid CO$_2$ at elevated pressure through the addition of TTIP.[192] In most cases, to obtain crystalline particles, the precipitate resulting from microemulsion synthesis must be isolated and calcined. On the other hand, Zhang et al.[193] showed that, in the presence of acids, the hydrolysis of titanium butoxide results in the formation of crystalline elongated particles. Similarly, researchers have hydrothermally treated an entire microemulsion solution to induce crystallization.[194,195] In another variation, Lin et al.[196] synthesized ∼5 nm crystalline anatase particles by a postsynthesis, in situ annealing at temperatures as high as 300 °C while maintaining a microemulsion for several hours (Figure 23). The size can be controlled in a narrow range (4−6 nm) by changing the surfactant/water ratio.

Biomolecules can also act as templates or initiators for the formation of inorganic nanoparticles with unique biomimetic structures[197] and can direct the growth of specific structures.[198] Natural proteins often exhibit unique morphologies in the nanometer size regime, which may act as templates for titania. These proteins usually work at neutral conditions. For instance, Yan et al.[199] used egg albumin proteins as templates in the preparation of 9 nm particles, and Sewell and Wright[200] utilized proteins derived from the diatom *Cylindrotheca fusiformis* to template the formation of titania with titanium(IV) bis-(ammonium lactato)dihydroxide as a precursor. Bansal et al.[201] described the direct synthesis of crystalline titania particles in the presence of proteins derived from the fungus *Fusarium oxysporum*. Jiang et al.[202] prepared titania particles by using protamine, and the authors postulated a mechanism in which electrostatic interactions between the positively charged
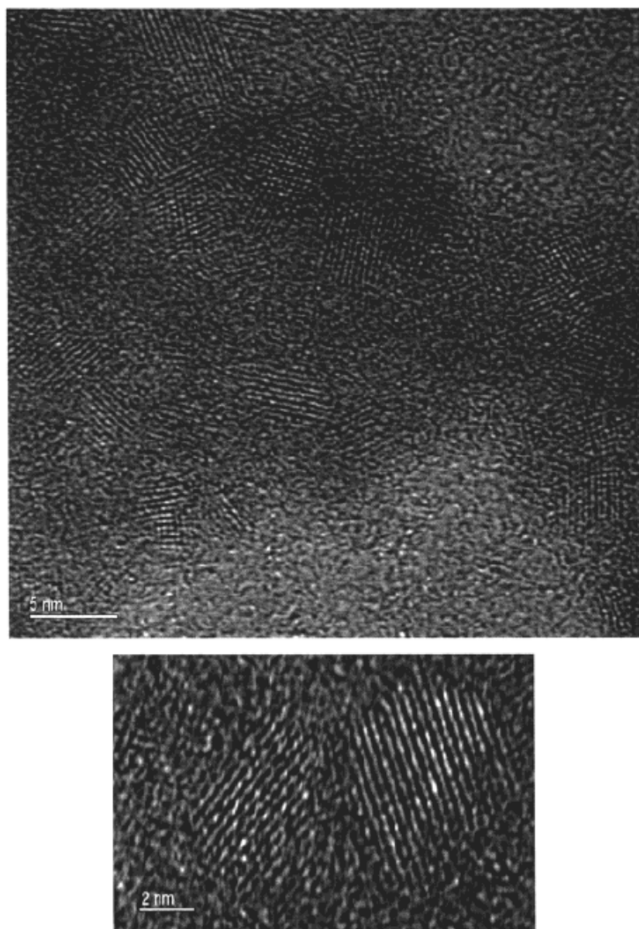
Figure 23. HRTEM images of crystalline titania particles obtained by a microemulsion technique with postsynthesis annealing in the microemulsion at 300 °C. Reprinted with permission from ref 196. Copyright 2002 American Chemical Society.

polyamine protein groups and the negatively charged titania precursors are the basis of the templating route. The titania materials prepared with these procedures are usually amorphous at room temperature, and their morphology is hardly controlled.

6.2. Hard Templates

Hard templating approaches utilize rigid inorganic or polymeric materials as templates, allowing for titania to be coated on the surface of a material to form shells once the template is dissolved or deposited into the channels of porous materials. For example, highly uniform titania hollow structures may be prepared by hydrothermally coating Cu_2O octahedral crystals with titania.[203] The synthesis utilizes the hydrolysis of TiF_4 precursor to form titania on the surface of the Cu_2O crystals along with the simultaneous etching of some of the Cu_2O layers by the HF formed in situ. Further acidic etching can completely dissolve the templating Cu_2O crystals, resulting in hollow titania cages that preserve the octahedral geometry in the absence of surfactants or stabilizing agents. The titania shells are polycrystalline and are composed of agglomerates of smaller crystallites, and their size can be controlled by varying the size of the templating Cu_2O nanocrystals. Similarly, hollow spheres were obtained by coating polystyrene particles with titanium butoxide, followed by a sol−gel approach to grow a titania layer on the surface.[204] After removal of the templating particles by

calcination or dissolution, hollow spheres of tunable diameter from 100 to 500 nm were obtained.

By use of an opposite templating strategy, titania precursors were infiltrated inside the pores created by ordered assemblies of monodisperse silica spheres.[205] Titania single crystals were then grown with TiF_4 and HF, conditions that reduces nucleation rate and allow a controlled slow growth of the crystals inside the template. By finally removing the silica template, mesoporous single crystals of anatase can be produced with advantageous properties of high surface area and conductivity and electron mobility due to their single-crystalline nature.

In a different approach, TiO_2−SiO_2 materials were prepared by sol−gel methods and, following a calcination process, titania nanoparticles can be trapped inside the mesoporous channels of the silica host.[206]

7. SUMMARY AND PERSPECTIVES

Titania remains one of the most-studied and most-used nanoscale materials, with a wide range of applications. Synthetic methods to prepare titania nanoparticles and nanocrystals with controlled size, shape, and phase are therefore of paramount importance to meet the expectations of the market and the increasing demand for titania with well-defined characteristics for advanced applications. Despite the great effort spent in the study of its structure, properties, and synthesis, there is still room for improvement in terms of quality of the products that are obtained by bottom-up approaches.

Historically, sol−gel methods were initially developed and titania nanoparticles were obtained in high yield and crystallinity after thermal treatments of the dried gels. Because of the poor properties of the as-prepared materials, however, hydrothermal and solvothermal methods were then applied. All these procedures have kept improving in recent years. Later, the development of surfactant-assisted nonhydrolytic routes have marked a huge improvement in this field, with the preparation of tailored titania nanostructures with increasing complexity, as well as size and shape control.

Still, many problems need to be solved. A clear correlation between synthetic parameters and the obtained products is still lacking, with several similar procedures resulting in drastically different results. Many reports of titania synthesis focus on the preparation and properties of the obtained products, with poor understanding of the parameters affecting the final size and composition. A few guidelines have been reported in this review, but systematic studies of how a particular parameter (temperature, pH, surfactant, etc.) influences the final structure and phase of a titania product are much needed. Strictly related to this point, experimental procedures to prepare materials with great control over size, shape, and phase are also lacking in the literature, with only a few appearing recently. It is surprising, for example, that the preparation of titania with high-surface-energy exposed facets has been reported only few years ago.[57] These procedures would be incredibly useful in correlating the structural parameters of titania with the performance of this important material for applications, such as photocatalysis, solar cells, batteries, etc.

To overcome some of the critical problems of past synthetic methods, new approaches are needed that provide exquisite control over the morphology, crystallinity, and phase purity of titania particles, and these are expected to provide the most opportunities to advance this field. Among the procedures reported in this review, surfactant-assisted solvothermal and

nonhydrolytic methods are the most promising approaches available to achieve the above-mentioned goals. It is expected that further developments in controlling the complexities of these synthetic approaches will result in the preparation of even more precisely tuned titania nanostructures, allowing the ideal geometries to be prepared for a given application.

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Notes

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Thomas R. Gordon received a B.S. in Chemistry from Lebanon Valley College in 2007 and a Ph.D. in Materials Chemistry from the University of Pennsylvania in 2013 under the supervision of Professor Christopher B. Murray. His graduate work concerned the synthesis of monodisperse oxide nanocrystals with controlled morphology for applications in photocatalysis and plasmonics. In 2013, he began as a postdoctoral fellow in the laboratory of Professor Raymond Schaak at Pennsylvania State University, where he investigated the preparation of hybrid nanoparticles to act as model systems for catalysis and optics.

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Dr. Christopher B. Murray received his B.Sc. degree with honors in Chemistry from St. Mary's University in Halifax (Nova Scotia, Canada) in 1988 before going on to the Massachusetts Institute of Technology, earning his Ph.D. in Physical/Inorganic Chemistry in 1995. He was a member of the research staff at IBM's T. J. Watson Research Center from 1995 to 2000 and manager of IBM's "Nanoscale Materials & Devices" department from 2000 to 2007. He currently holds the Richard Perry University Professorship in Chemistry and Materials Science at the University of Pennsylvania (Philadelphia, PA), where his research focuses on the preparation, characterization, and integration of nanomaterials. Chris has authored more than 100 scholarly articles, and he is an inventor on more than 25 patents in the area of nanoscale materials and devices.

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