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Keywords:	Titanates, Sol-gel processes, Ionic liquids, Anatase, Solvothermal



The Synthesis of Anatase TiO₂ Nanoparticles via Solvothermal Method using Ionic Liquid as Additive

Hechun Lin,^[a] Peter W. de Oliveira,^[a] Ingrid Grobelsek,^[a] Aude Haettich,^[a] and Michael Veith^{[a,b]*}

Dedicated to Professor Rüdiger Kniep on the Occasion of his 65th Birthday

Keywords: Titanates; Sol-gel processes; Ionic liquids; Anatase; Solvothermal

Abstract. The solvothermal reactions of Ti(OⁱPr)₄ in alcohol using ionic liquid as additive were investigated. In the presence of [BMIM][Cl], [BMIM][Br], [BMIM][NTf₂], [BMIM][SO₃Me], [BMIM][SO₄Me], or [BMIM][OTf] (BMIM = 1-Butyl-3-methylimidazolium), pure anatase nanoparticles were obtained. The controlled hydrolysis of Ti(OⁱPr)₄ in the presence of ionic liquids to form titanium oxo clusters plays a key role in the formation of anatase nanostructures, and ionic liquids can be repeatedly used to synthesize anatase nanoparticles. However, in the presence of [BMIM][PF₆], [BMIM]₂[Ti(OH)₆] was obtained via an anion exchange reaction.

Introduction

Titanium oxide (TiO₂) nanomaterials have received significant attention because of their numerous applications such as photocatalysts, pigments, photovoltaic cells, gas sensors, etc. [1]. The physical and chemical properties of TiO₂ can be controlled by its particle size, morphology, and crystalline modification. Many methods have been used to synthesize TiO₂ nanomaterials, such as sol-gel, hydrothermal, solvothermal, sonochemical, chemical vapour deposition, electrodeposition, etc.

Room temperature ionic liquids, due to their special properties, such as negligible vapour pressure, low toxicity, low melting points, high chemical and thermal stability and wide electrochemical window [2,3], may be seen as a tool with potential for use in sustainable processes such as solvent replacement [4,5], in catalytic reactions [6,7], in electrochemistry [8], in biocatalysis [9-11] and in the synthesis of nanomaterials [12-16]. Much research has been focused on the synthesis of TiO₂ nanomaterials. Hollow TiO₂ amorphous microspheres

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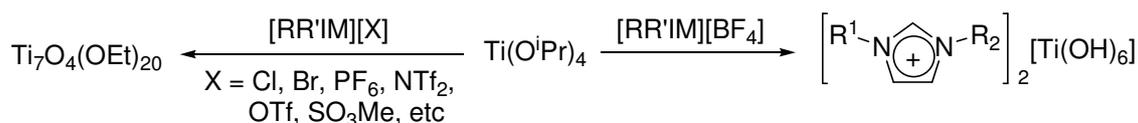
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3 [17], anatase nanoparticles [18-28], anatase mesoporous monoliths [29], rutile nanostructures
4 [30-33] and TiO₂ (B) in anatase nanopaticles [34] have been synthesized in ionic liquids.

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7 The growth of TiO₂ nanostructures in ionic liquids is a complex process. Ionic liquids are
8 normally considered to act as reaction media, templates or surfactants. Dionysiou et al.
9 pointed out that the use of 1-butyl-3-methyl-imidazolium hexafluorophosphate ([BMIM][PF₆])
10 in the synthesis of anatase mesoporous nanoparticles induces controlled hydrolysis of titanium
11 alkoxide, but there was no obvious chemical bond formation between [BMIM][PF₆] and
12 titanate [19]. However, Liu et al. found the formation of an ionic liquid-stabilized polyanion
13 complex in the microwave-assisted synthesis of size-controlled anatase nanoparticles using
14 [BMIM][BF₄] as medium [22]. Yang et al. proposed that the self organization ability of
15 [BMIM][BF₄] or [BMIM][PF₆] lead to anatase crystalization by condensation of the Ti-OH
16 groups of hydroxoylated titanium compound in the thermal aneannealing process [26]. Yu et
17 al. suggested that Ti⁴⁺ ions are all octahedrally coordinated by ligands like [OH]⁻ and [Cl]⁻
18 through formation of chloride complexes of the type [Ti(OH)_mCl_n]₂⁻ (m + n = 6) in the
19 synthesis of rutile TiO₂ nanorods in [BMIM][Cl] with TiCl₄ as precursor [31]. Using FTIR,
20 Zhai et al. confirmed the formation of a bidentate chelating complexation between the
21 carboxylic functional group of 1-methylimidazolium-3-acetate chloride ([AcMIM][Cl]) and
22 titanate in synthesis of rutile TiO₂ [32]. Most recently, Zheng et al. proposed that the
23 interaction between imidazolium cation and TiO₆ octahedra could be a decisive factor for the
24 formation of the rutile phase, which is beneficial for the catenarian nuclei via edge-sharing
25 polycondensation between TiO₆ octahedra due to the mutual π-staking between aromatic rings
26 [33]. HF and H₂SO₄ were used as additives to inhibit the phase transformation in
27 hydrothermal synthesis of anatase nanocrystals assisted by ionic liquid [25].

28
29
30 In a recent article, we have reported about the early hydrolysis stages of Ti(OⁱPr)₄ in
31 imidazolium based ionic liquids/ethanol mixtures [35]. We found that most ionic liquids such
32 as [BMIM][Cl], [BMIM][Br], [BMIM][PF₆], [BMIM][N(Tf)₂] (Tf: SO₃CF₃), [BMIM][OTf]
33 (Tf: COCF₃) and [BMIM][NCN₂], etc, as additives controlled the hydrolysis of Ti(OⁱPr)₄ to
34 form Ti₇O₄(OEt)₂₀. There was no obvious chemical bonding between ionic liquid and titanium
35 complex as indicated by NMR spectroscopy. In contrast, an anion exchange reaction in [BF₄]⁻
36 based ionic liquids to form hexahydroxotitanate salts was found (Scheme 1). In this paper, we
37 describe the further polycondensation process under solvothermal conditions [36-47]. The
38 effects of water concentration, different alcohols, and ionic liquids on the products were
39 investigated in detail. Pure anatase nanoparticles were obtained, and some ionic liquids can be
40 used again up to five times to give rise to anatase in quantitative yields.



Scheme 1

Experimental Section

All chemicals were used as received. $\text{Ti}(\text{O}^i\text{Pr})_4$ was distilled under vacuum before use. $[\text{BMIM}][\text{Cl}]$, $[\text{BMIM}][\text{Br}]$, $[\text{BMIM}][\text{PF}_6]$, $[\text{BMIM}][\text{BF}_4]$, $[\text{BMIM}][\text{NTf}_2]$ were synthesized according to literature method [48]. $[\text{BMIM}][\text{SO}_3\text{Me}]$, $[\text{BMIM}][\text{SO}_4\text{Me}]$, and $[\text{BMIM}][\text{OTf}]$ were received from IoLiTec GmbH. Water contents of alcohol were titrated by Karl Fischer method.

2.84 g $\text{Ti}(\text{O}^i\text{Pr})_4$ (10 mmol) was added dropwise to the solution of ionic liquid (20 mmol) in ethanol (26 g) at room temperature. Stirring was performed at room temperature and it was refluxed for 4 hours to form $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$. Subsequently, the solution was transferred to a 250 mL Teflon flask and cured in an autoclave or, without pre-curing process, the mixture was cured directly in the autoclave. The temperature was raised up at a ramp rate of $4.4^\circ\text{C}/\text{min}$ to 210°C . The whole hydrothermal process took 2.75 hours or 12 hours. The solution was cooled down gradually to room temperature in the autoclave. The precipitated solids were separated via centrifugation. The ionic liquid part can be re-used via rotationally evaporating off the low boiling component under reduced pressure (10^{-2} atm). The products were washed for five times with ethanol and were freeze-dried under 10^{-2} atm using water as solvent. There were no obvious absorption bands of ionic liquids in the FTIR spectra in most of the samples. The reactions in other alcohols such as propanol, butanol, or iso-propanol were run similarly to this procedure. For comparison, $\text{Ti}(\text{O}^i\text{Pr})_4$ has also been cured in the absence of ionic liquids. The samples were labeled as SN where N is a progressive integer.

$\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ was synthesized using $[\text{BMIM}][\text{Cl}]$ as additive. 2.84 g $\text{Ti}(\text{O}^i\text{Pr})_4$ (10 mmol) was added drop-wise to the solution of $[\text{BMIM}][\text{Cl}]$ (3.49 g, 20 mmol) in ethanol (11.4 g, less 0.1% water) under magnetic stirring at room temperature in an open flask. After stirring for 1 hour at room temperature obtaining a turbid solution, the temperature was raised up to reflux to solve all precipitates and to obtain a clear liquid. Stirring was continued for 4 hours and then the low boiling components were distilled off. The liquid was redissolved in CH_3CN and EtOAc under reflux and filtered with a fine filter paper to give rise to the mother liquor. This was kept at room temperature over night. Colorless crystals precipitated, which were grown further in a refrigerator at -30°C for one day. Finally, the mother liquor was decanted off. The

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3 solids were washed with CH₃CN for three times and dried with N₂ flow to give rise to 1.27 g
4 (70%) Ti₇O₄(OEt)₂₀. Subsequently, the obtained Ti₇O₄(OEt)₂₀ was solved in ethanol (26 g,
5 with less than 0.1% H₂O or 2% H₂O, respectively) and was cured in an autoclave for 12 hours
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7 at 210°C to give rise to anatase nanoparticles.
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10 Powder X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 powder
11 diffractometer unit, using Cu K α radiation ($\lambda=0.154$ nm) operating at 40 kV and 40 mA. A
12 position sensitive detector (LynxEye) based on Bruker AXS' compound silicon strip
13 technology was applied. The patterns were recorded from 3° to 90° in 2 θ with a 2 θ scan step
14 size of 0.02°. For clarity, the low angle region of pure anatase samples is not shown in the
15 figures. For all powders glass sample holders were used. The structural refinement of anatase
16 and profile analysis of related powder diffraction patterns were carried out with the program
17 TOPAS [49]. In this program, the line profile shapes are described by convoluting the X-ray
18 source emission profile with the instrument aberrations and physical properties of the sample
19 (fundamental parameters convolution-based approach) [50]. The mean crystallite sizes were
20 calculated by the Scherrer equation (Scherrer constant $k = 1$). The integral broadness-based
21 volume-weighted calculation assuming intermediate crystallite-size broadening was modelled
22 by a Voigt function. Transmission electron microscope (TEM) and high-resolution
23 transmission electron microscope pictures (HRTEM) were obtained by use of a JEM-3010
24 electron microscope. Nitrogen porosimetry was performed on a Quantachrome Autosorb6B
25 Instrument. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation.
26 FTIR spectra were measured on Bruker Tensor 27 Fourier Transform Infrared. Raman
27 spectra were obtained from Lab Ram Aramis (Horiba Jobin Yvon).
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43 44 **Results and Discussion**

45 *The synthesis of TiO₂ in [BMIM][Cl] using EtOH as solvent*

46 Ti(OⁱPr)₄ was firstly hydrolysed in the presence of 2 eq. [BMIM][Cl] with ethanol as
47 solvent in the presence of less than 0.1% water in the alcohol. After stirring at room
48 temperature for 1 hour and refluxing for 4 hours, a clear solution was obtained and
49 Ti₇O₄(OEt)₂₀ was formed. The mixture was transferred to a Teflon flask and hydrothermally
50 cured for 2.75 hours to give rise to white solids of sample S1. Besides two peaks at 2 θ values
51 of 8.25° and 16.21°, the formed product showed a powder X-ray diffraction (PXRD) pattern
52 comparable to anatase of low range order (Fig. 1b-S1) with mean crystallite sizes between 2
53 and 4 nm. The two reflections at low angles could not be assigned to any available JCPDS
54 (Joint Committee on Powder Diffraction Standards) pattern. They were also different to the
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3 result of Smarsly et al., who obtained amorphous TiO_2 with an additional signal at about $2\theta =$
4 12° during the synthesis of rutile TiO_2 via extraction method with $^i\text{PrOH}$ [30]. In the TEM
5 image no crystalline fractions could be identified (Fig. 2a). The sample has also been analysed
6 with FTIR and Raman spectra. In the FTIR spectrum (Fig. 3a), the absorption bands at 1111,
7 1165, 1382, 1465, 1569, 2873, 2963, 3107, 3147 cm^{-1} belong to $[\text{BMIM}]^+$. However, the
8 absorption at 3107 and 3147 cm^{-1} were different from that in bulk $[\text{BMIM}][\text{Cl}]$ [51]. The band
9 centered around 3257 cm^{-1} is assigned to the hydroxyl group of Ti-O-H, and the absorption
10 centered around 1642 cm^{-1} is associated with the deformation vibration of H-O-H bonds from
11 the physico-sorbed water [52]. In the Raman spectrum (Fig. 3b), there is no obvious typical
12 absorption of anatase, however, the absorption bands at 163, 185, 272, 284, 384, 447, 673,
13 700, 825 cm^{-1} are similar to those of titanate [53]. These results indicate the formation of the
14 titanate and the interaction between the imidazolium ring and the titanate. By prolonging the
15 curing time to 12 hours, crystallized TiO_2 (anatase) was obtained with a mean crystallite size
16 of 9 nm. The diffraction pattern shows reflections of anatase [54] (Fig. 1a, S2). No peaks for
17 any other phases were detected in the pattern. TEM image of sample S2 (Fig. 2b) shows that
18 almost spherical and accordingly cube-like particles were formed in agreement with the ratio
19 of the calculated column heights (crystallite size broadening) of the (004):(020) X-ray
20 reflections of 7:8. If the mixture was cured directly under the solvothermal conditions without
21 the pre-curing process, the resulted powder was similar to that of sample S2 but with a
22 slightly lower mean crystallite size of 6 nm (Fig. 1a-S3, Fig. 2c). The presence of 2 eq.
23 $[\text{BMIM}][\text{Cl}]$ was a prerequisite for the formation of crystalline monophasic anatase
24 nanoparticles. In the presence of 0.5 eq. (sample S4) or 1 eq. $[\text{BMIM}][\text{Cl}]$ (sample S5),
25 similarly to sample S1 only porous products with broad and weak X-ray reflections with non-
26 identifiable peaks at 2θ values of $\sim 7.97^\circ$ and $\sim 15.77^\circ$ were obtained (Fig. 1b-S4, 5, TEM
27 image: Fig. 2d, e).
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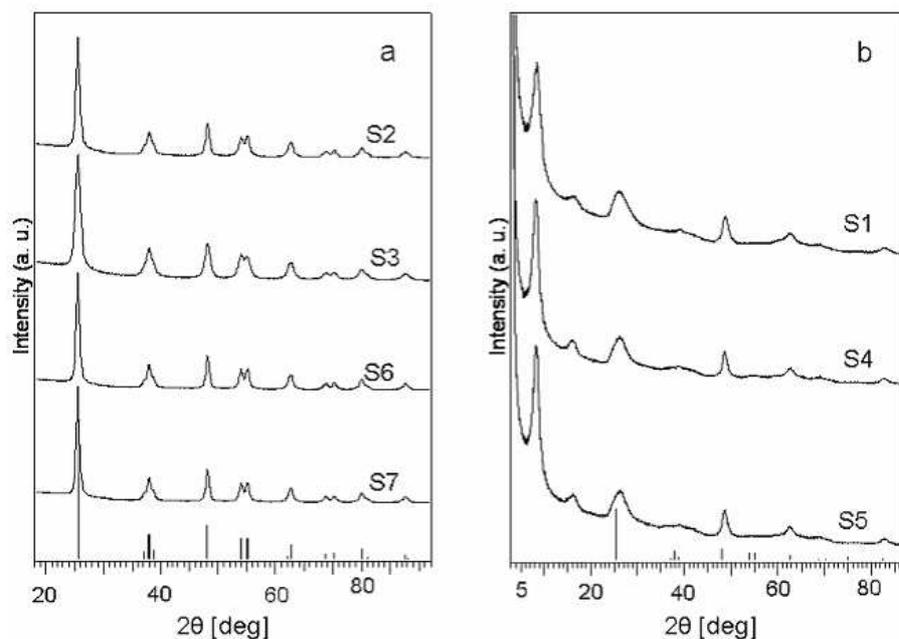


Figure 1. Powder X-ray diffraction (PXRD) patterns of TiO_2 particles synthesized at various conditions. S1: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g), refluxed for 4 h, then cured for 2.75 h at 210°C in the autoclave. S2: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g), refluxed for 4 h, then cured for 12 h at 210°C in the autoclave. S3: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g), cured for 12 h at 210°C in the autoclave. S4: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.005 mol), ethanol (26 g), cured for 12 h at 210°C in the autoclave. S5: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.01 mol), ethanol (26 g), cured for 12 h at 210°C in the autoclave. S6: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g, 2% water), cured for 12 h at 210°C in the autoclave. S7: $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g, 5% water), cured for 12 h at 210°C in the autoclave.

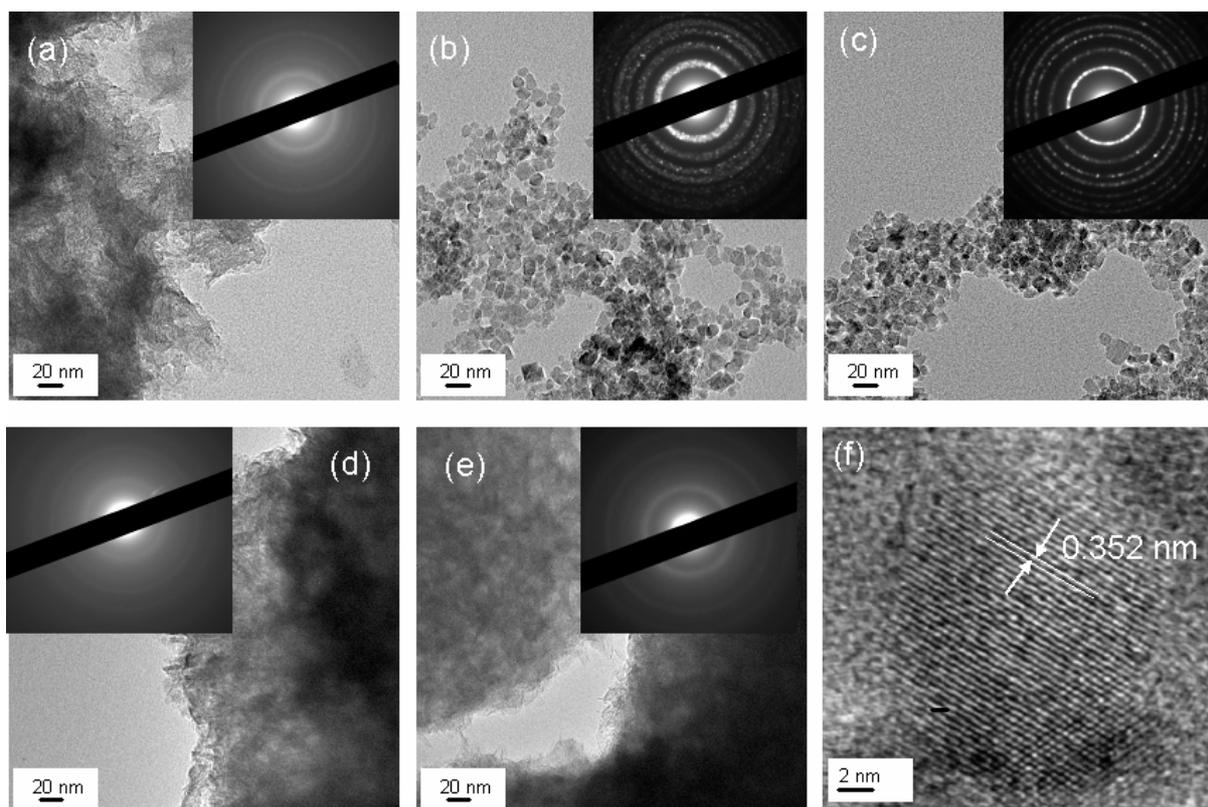


Figure 2. TEM images of TiO₂ particles in different samples S1-S5. a) S1, b) S2, c) S3, d) S4, e) S5, f) HRTEM of S3. Insets are selected area electron diffraction patterns.

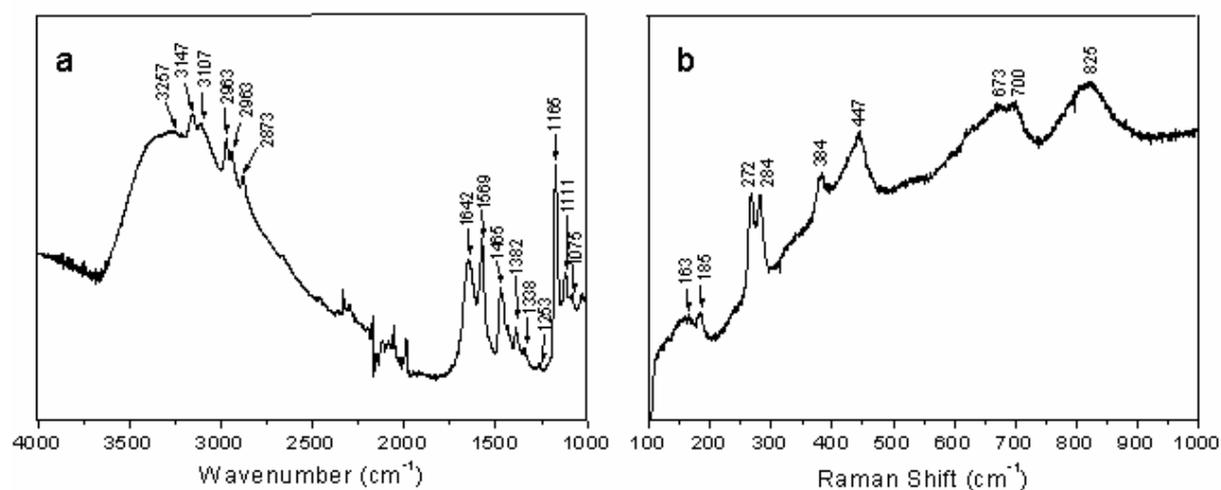


Figure 3. (a) FTIR spectrum of sample S1; (b) Raman spectrum of sample S1.

In the next steps, we checked the effect of water concentrations in alcohols to the synthesis. Increasing the water content to 2% (S6) or 5% (S7) produced single-phase nanoscaled anatase powders with a slightly bigger particle size (see Table 1) than in case of the samples S2 and S3. As can be seen from the TEM images in Fig. 4, the presence of 2% water gave rise to cube-like anatase nanoparticles with a calculated crystallite size-ratio of (004):(020) planes of

nearly 8 : 8 in Sample S6 and 9 : 10 in Sample S7. The particles shown in the HRTEM image are placed on copper grid parallel to [101] direction. The surface area (S_{BET}) was estimated by BET method. The S_{BET} is found in a range from 120 to 163 $\text{m}^2\cdot\text{g}^{-1}$ (Table 1). In agreement with the X-ray data and TEM images, the increased concentration of H_2O led to a lower surface area. Crystallite sizes and BET surface areas of the Samples S1-S7 in dependency of preparation conditions are listed in Table 1.

Table 1. Preparation conditions, Crystallite sizes, and BET surface areas of TiO_2 .^a

Sample	water contents in alcohol	crystallite size (nm)	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)
S1	< 0.1% ^b	-	-
S2	< 0.1% ^c	9	143
S3	< 0.1% ^d	6	163
S4	< 0.1% ^{d,e}	-	-
S5	< 0.1% ^{d,f}	-	-
S6	2% ^d	10	123
S7	5% ^d	11	120

^a $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), ethanol (26 g) b) Refluxed for 4 h, then cured for 2.75 h at 210°C in the autoclave. c) Refluxed for 4 h, then cured for 12 h at 210°C in the autoclave. d) Without pre-curing process, cured directly for 12 h at 210°C in the autoclave e) $[\text{BMIM}][\text{Cl}]$: 0.005 mol. f) $[\text{BMIM}][\text{Cl}]$: 0.01 mol.

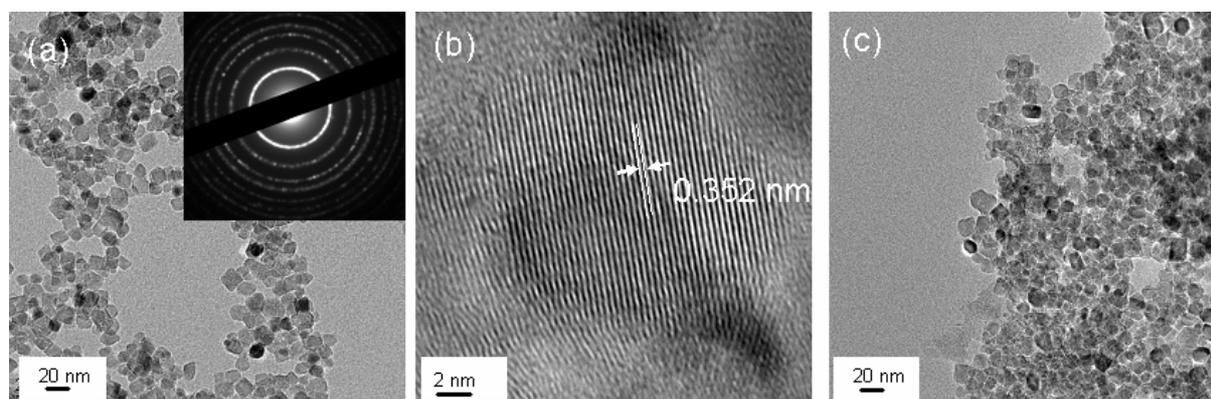


Figure 4. TEM images of different TiO_2 samples S6 and S7. (a) S6; (b) HRTEM of S6; (c) S7. Inset is a selected area electron diffraction pattern,

The synthesis of anatase in $[\text{BMIM}][\text{Cl}]$ using other alcohols as solvents

Many different alkoxy titanium clusters have been reported in the literature [55,56]. It seemed interesting to see if the addition of ionic liquids has an impact on the hydrolysis of

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3 Ti(OⁱPr)₄ in other alcohols to form different titanium clusters. We therefore hydrolyzed
4 Ti(OⁱPr)₄ in alcohols such as PrOH, ⁱPrOH, or BuOH. Titanium oxo clusters were
5 successfully formed as derived from IR, but an exact specification of the structure was not
6 possible since no crystals suitable for the single crystal X-ray diffraction analysis were
7 obtained. We also performed the solvothermal reactions without the pre-curing step. Using
8 PrOH or ⁱPrOH as solvent with less than 0.1% water produced, besides anatase at least one
9 more phase with broad X-ray reflections amongst others at 2θ values of 8.01° and 15.95°. As
10 can be seen from the X-ray patterns of Fig. 5b, if Pr(OH) was used, the main phase in the end
11 product was anatase (S8). In the case of ⁱPr(OH) (S9) a high content of a non-identified
12 compound was obtained. Increasing the water content to 2%, monophasic anatase
13 nanoparticles were formed; the PXRD patterns are summarized in Fig. 5a. PrOH or BuOH
14 (samples S10 and S12) gave rise to mean crystallite sizes of 9 nm and 8 nm of anatase,
15 respectively. The difference of the column heights ratio of the (004):(020) reflections of 6:8 in
16 S10 and 5:7 in S12 leads to almost spherical particles. However, in the presence of ⁱPrOH,
17 bipyramidal nanoparticles were obtained (Fig. 6b, d) with a mean crystallite size of 13 nm and
18 a crystallite size ratio of (004):(020) reflexes of 20:8. As shown in the HTEM image in Fig.
19 6d, the particles are oriented on the copper grid parallel to [101] direction. The results of the
20 different preparation characteristics are summarized in Table 2.
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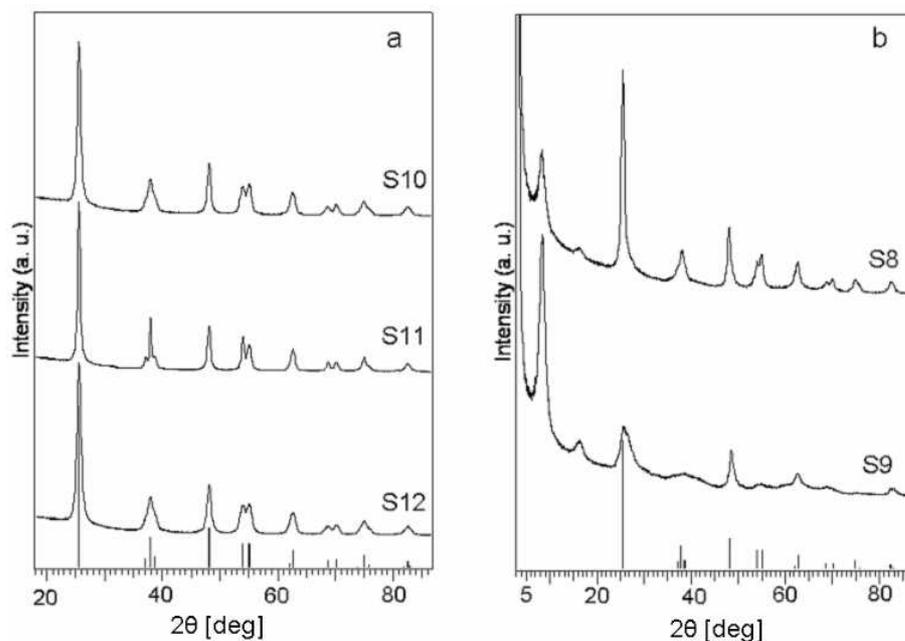


Figure 5. Powder X-ray diffraction (PXRD) patterns of TiO_2 particles synthesized at various conditions (samples S8-S12). $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), alcohol (26 g), cured for 12 h at 210°C in the autoclave. S8: PrOH (26 g); S9: $^i\text{PrOH}$ (26 g); S10: PrOH (26 g, 2% water); S11: $^i\text{PrOH}$ (26 g, 2% water); S12: BuOH(26 g, 2% water).

Table 2. Preparation conditions, Crystallite sizes, and BET surface areas of TiO_2 .^a

Sample	alcohols	water contents	Crystallite size (nm)	SBET ($\text{m}^2 \cdot \text{g}^{-1}$)
S8	PrOH	< 0.1%	8	-
S9	$^i\text{PrOH}$	< 0.1%	-	-
S10	PrOH	2%	9	134
S11	$^i\text{PrOH}$	2%	13	102
S12	BuOH	2%	8	146

^a $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.01 mol), $[\text{BMIM}][\text{Cl}]$ (0.02 mol), alcohol (26 g), without the pre-curing process, the mixtures were cured directly for 12 h at 210°C in the autoclave.

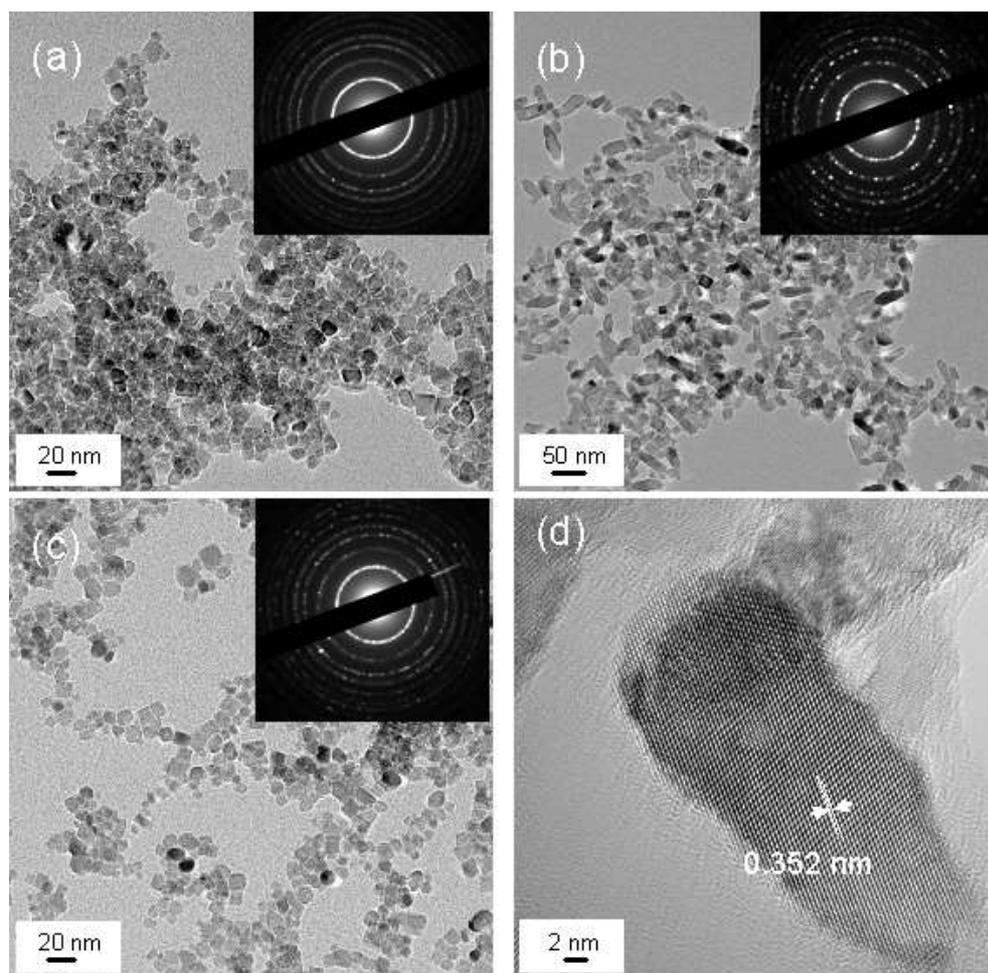


Figure 6. TEM images of TiO₂ particles from samples S10-S12. (a) S10; (b) S11; (c) S12; (d) HTEM image of S11. Insets are selected area electron diffraction patterns.

The synthesis of TiO₂ in other ionic liquids

Finally, we investigated the hydrothermal reactions of Ti(OⁱPr)₄ with other ionic liquids. As can be seen from the above results, water concentration strongly influences the end product. 2% of water content is enough for the complete polycondensation of the titanium precursors. Herein, we used EtOH containing 2% water as solvent. Without the pre-curing procedure, the mixture was cured directly under the solvothermal condition. The results are shown in Table 3 and the correspondent PXRD patterns and TEM images are assembled in Fig. 7 and Fig. 8, respectively. In the presence of [BMIM][Br], [BMIM][NTf₂], [BMIM][SO₃Me], [BMIM][SO₄Me], or [BMIM][OTf], which mediated the hydrolysis of Ti(OⁱPr)₄ to form intermediate Ti₇O₄(OEt)₂₀ under the reflux condition, pure crystalline single-phase anatase nanoparticles were generated. The different crystallite sizes achieved are listed in Table 3. In the presence of [BMIM][BF₄] (S19), which has been found to form [BMIM]₂[Ti(OH)₆] via anion exchange reaction under the reflux condition, only a small amount of anatase was

obtained with a mean crystallite size of 9 nm. The smallest sizes, however with a mean diameter of 4 nm, had anatase particles generated in presence of [BMIM][SO₄Me]. Surprisingly, in the presence of [BMIM][PF₆], although Ti₇O₄(OEt)₂₀ was obtained under the reflux condition, no solid precipitated but a biphasic liquid was obtained. The low boiling point components were evaporated to give rise to a liquid, which was analysed with NMR to show a new imidazolium compound. The product was separated via re-crystallization from CH₃CN/EtOAc for two times. The obtained needle-like crystals were identified as [BMIM]₂[Ti(OH)₆] using single crystal X-ray diffraction [35]. For comparison, the Ti(OⁱPr)₄ was firstly hydrolysed under the reflux conditions to form Ti₇O₄(OEt)₂₀, and then cured under solvothermal conditions. Ti₇O₄(OEt)₂₀ was further hydrolysed to carry out the anion exchange reaction to form [BMIM]₂[Ti(OH)₆] as well. These results indicated that [BMIM]₂[Ti(OH)₆] was thermally more stable than [BMIM][PF₆]. The reason for this anion exchange reaction under the solvothermal condition might have to do with the less stable [PF₆]⁻ anion, which could lose fluoride in the reaction conditions [57].

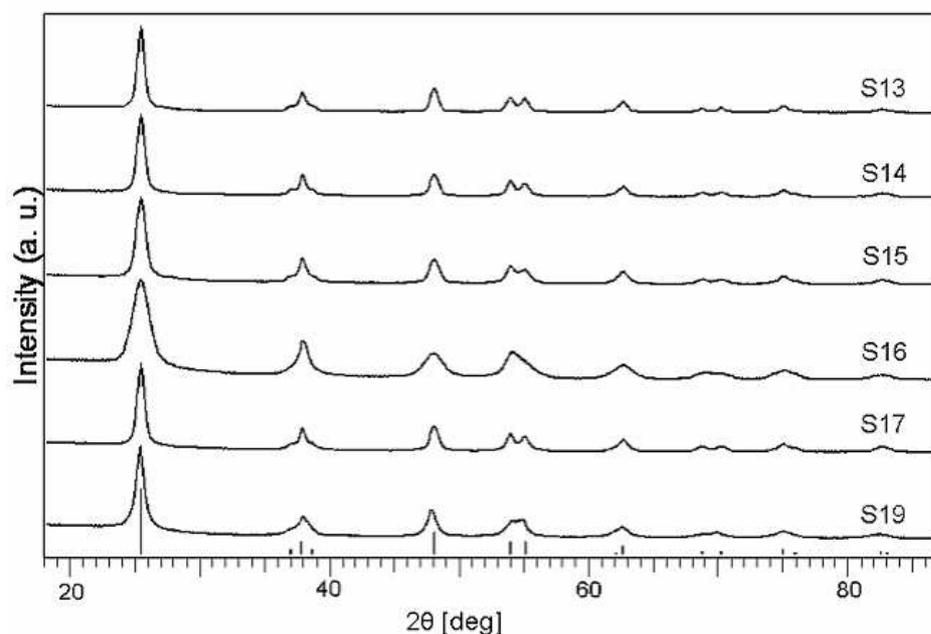


Figure 7. Powder X-ray diffraction (PXRD) patterns of TiO₂ particles synthesized at various conditions. Ti(OⁱPr)₄ (0.01 mol), ionic liquids (0.02 mol), EtOH (26 g, 2% H₂O), cured for 12 h at 210°C in the autoclave. S13: [BMIM][Br]; S14: [BMIM][NTf₂]; S15: [BMIM][SO₃Me]; S16: [BMIM][SO₄Me]; S17: [BMIM][OTf]; S19: [BMIM][BF₄].

Table 3. Preparation conditions, Crystalline sizes, and BET surface areas of TiO₂.^a

Sample	Ionic liquids	Crystallite size [nm]	BET area (m ² /g)
S13	[BMIM][Br]	11	123
S14	[BMIM][NTf ₂]	10	119
S15	[BMIM][SO ₃ Me]	8	148
S16	[BMIM][SO ₄ Me]	4	179
S17	[BMIM][OTf]	10	128
S18	[BMIM][PF ₆]	-	-
S19	[BMIM][BF ₄]	7	-

a) Ti(OⁱPr)₄ (0.01 mol), ionic liquid (0.02 mol), ethanol (26 g, 2% H₂O). The mixtures were cured directly for 12 h at 210°C in the autoclave.

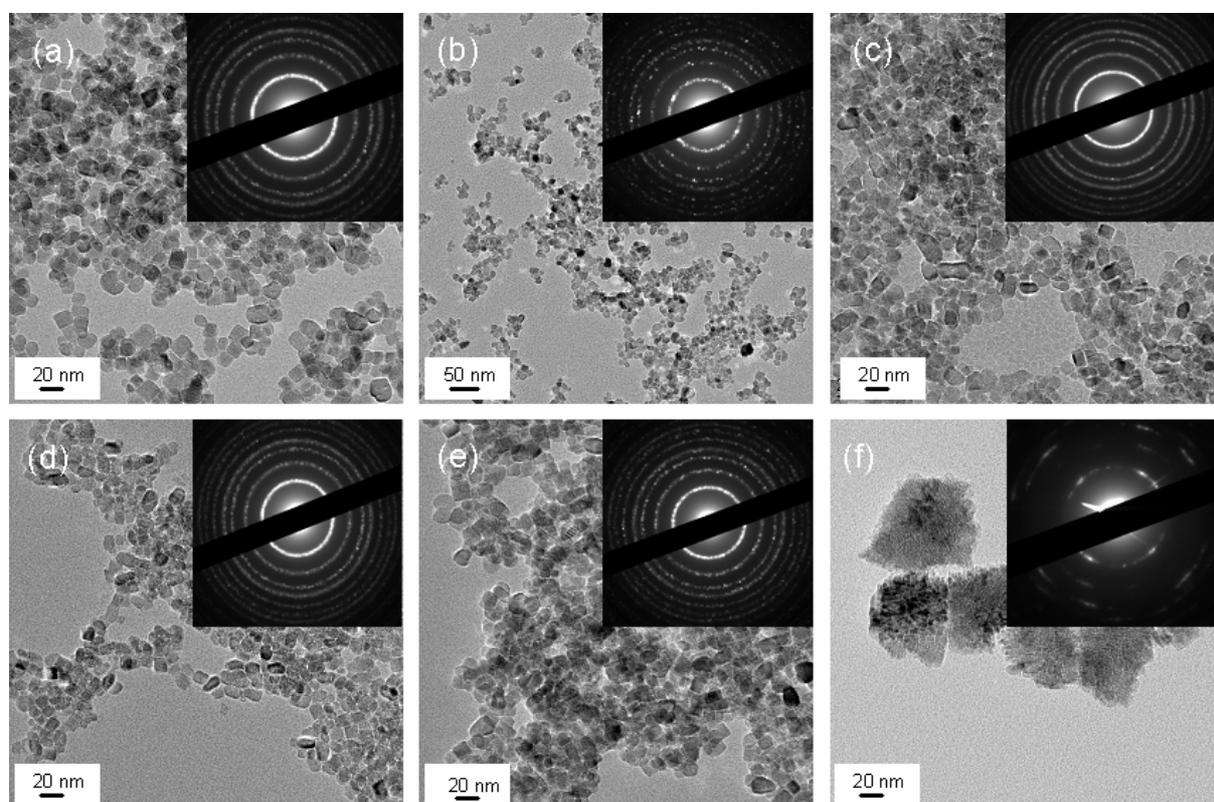


Figure 8. TEM images of TiO₂ particles. (a) S13; (b) S14; (c) S15; (d) S16; (e) S17; (f) S18. Insets are selected area electron diffraction patterns.

As can be seen from the above results, most of the tested ionic liquids gave rise to pure anatase nanoparticles, except [BMIM][PF₆] and [BMIM][BF₄] which both have complexed fluoride anions and thus are susceptible to loose fluoride in the reaction. F⁻ has been found in these two reaction mixtures via F¹⁹ NMR analysis. For comparison, we carried out the same solvothermal reaction of Ti(OⁱPr)₄ in the absence of ionic liquids. In this case, white powders

were obtained. However, they had a lower crystallinity compared to the products in the presence of ionic liquids as shown in the XRD pattern (Fig. 9, S20) and TEM image (Fig.10a). We have found that $Ti_7O_4(OEt)_{20}$ can be obtained in good yields via the controlled hydrolysis of $Ti(O^iPr)_4$ using ionic liquids as further components. To know if titanium oxo clusters play a key role in the formation of nanostructures, $Ti_7O_4(OEt)_{20}$ was separated via crystallization and introduced to the solvothermal reaction afterwards. Using EtOH with less than 0.1% H_2O (S21) or 2% H_2O (S22) as solvent gave rise to pure crystalline single-phase anatase nanoparticles as well. The correspondent PXRD-patterns and TEM images are shown in Fig. 9 and Fig. 10, respectively. With a lower water content in the alcohol, the resulting crystallite size of the particles was nearly half (6 nm) of that at higher water content (11 nm). The physical characteristics of the so obtained TiO_2 powders are summarized in Table 4. They had similar physical characteristics to S3 and S6 (see before). Taking into account all our results it seems clear that the controlled hydrolysis of $Ti(O^iPr)_4$ by ionic liquids passes through the formation of intermediate $Ti_7O_4(OEt)_{20}$. Thus, this compound plays a key role in the formation of anatase nanostructures. The more condensed titanium clusters seem to improve the formation of the anatase nanostructure. Water concentration also has effect on the final products. The system itself cannot produce water. It needs sufficient water to let the precursor polycondense. When it has less amount of water, the reaction gives rise to smaller crystallite size TiO_2 or only leads to partially condensed products. 2% water is enough for polycondensation observed in our set-up.

Table 4. Preparation conditions, Crystallite sizes, and BET surface areas of TiO_2 .^a

Sample	precursor	Water contents	Particle size	BET area (m^2/g)
S20	$Ti(O^iPr)_4$	<0.1%	4	-
S21	$Ti_7O_4(OEt)_{20}$	<0.1%	6	144
S22	$Ti_7O_4(OEt)_{20}$	2%	11	153

a) The mixtures were cured directly for 12 h at 210°C in the autoclave. S20: $Ti(O^iPr)_4$ (0.01 mol), ethanol (26 g); S21: $Ti_7O_4(OEt)_{20}$ (1.27 g), ethanol (26 g); S22: $Ti_7O_4(OEt)_{20}$ (1.27 g), ethanol (26 g, 2% H_2O).

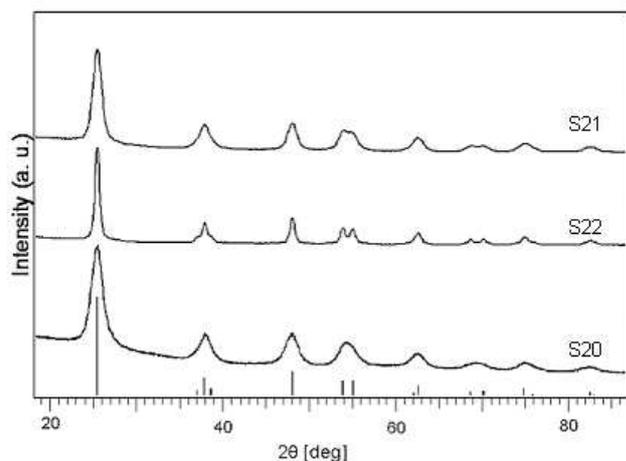


Figure 9. Powder X-ray diffraction (PXRD) patterns of TiO_2 particles synthesized at various conditions. The mixtures were cured directly for 12 h at 210°C in the autoclave. S20: $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.84 g), EtOH (26 g); S21: $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ (1.27 g), EtOH (26 g). S22: $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ (1.27 g), EtOH (26 g, 2% H_2O);

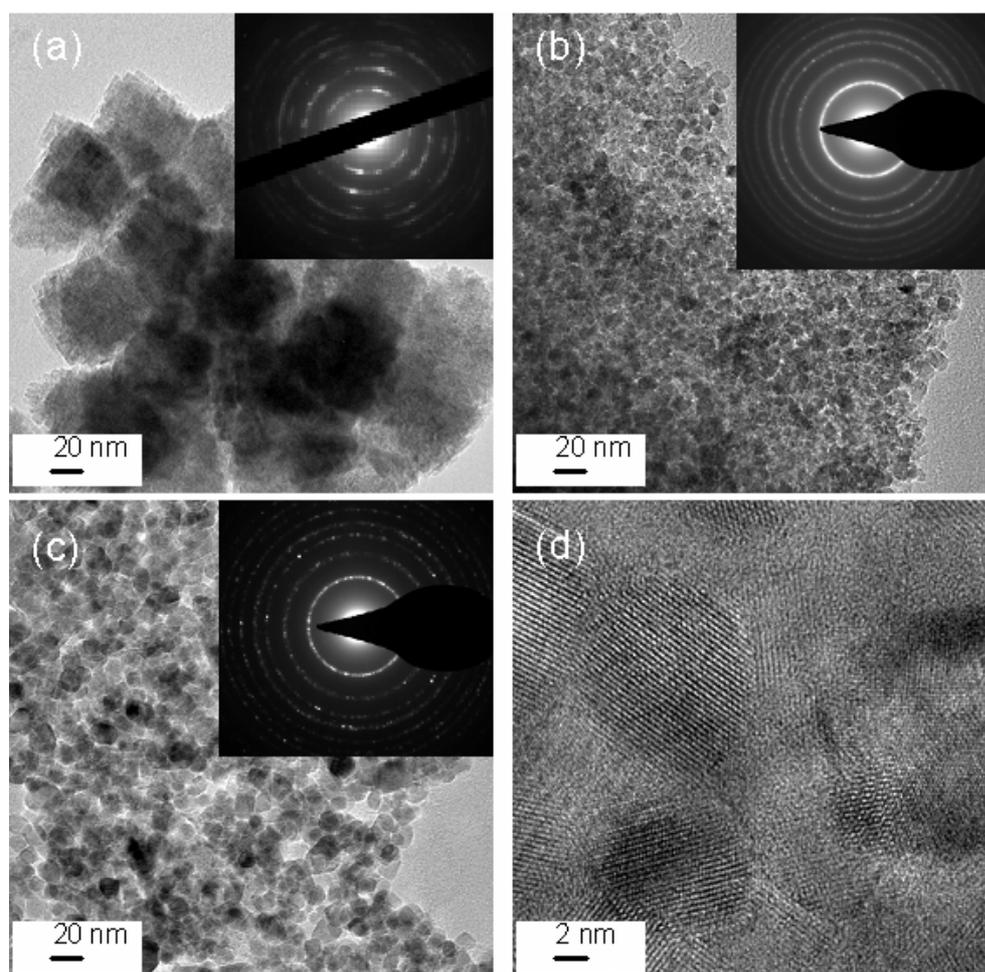


Figure 10. TEM images of TiO_2 particles. (a) S20; (b) S21; (c) S22; (d) HRTEM of S22. Insets are selected area electron diffraction patterns.

Re-use of ionic liquids

Many TiO₂ nanomaterials synthesis methods using ionic liquids as media have been reported. However, there were only rare reports about the repeated use of ionic liquids in the synthesis of TiO₂ until now. This may be due to the fact that it is difficult to separate the ionic liquids from the reaction system or ionic liquids may have been decomposed during the reactions. **In our method, ionic liquids such as [BMIM][Cl], [BMIM][Br], or [BMIM][NTf₂] were stable in the solvothermal conditions.** After the end of the process, the mixture includes TiO₂ (anatase), ionic liquids, and alcohols. TiO₂ can be easily separated by centrifugation and ionic liquids can be recollected for further use. For example we have found that [BMIM][Cl] and [BMIM][NTf₂] can be repeatedly used up to five times with ethanol (2% water) as solvent to give rise to pure anatase nanoparticles in quantitative yields.

Conclusion

We carried out the solvothermal reactions of Ti(OⁱPr)₄ in alcohol using ionic liquid as additive. In the presence of [BMIM][Cl], we performed the solvothermal reactions in different water concentration and different alcohols. The system itself cannot produce water. 2% water was enough for the complete polycondensation of the precursor. Spheric or cube-like anatase nanoparticles were obtained; except the reaction in PrOH gave rise to bipyramidal nanoparticle. We have also investigated the effect of different cations to the reactions. Using EtOH (2% water) as solvent, most ionic liquids gave rise to anatase nanoparticles with a small variation of crystallite size. Two exceptions were the reactions in [BMIM][BF₄] or [BMIM][PF₆]. The former carried out the anion exchange reaction under the reflux condition to form [BMIM]₂[Ti(OH)₆], and the latter led to the same reaction under solvothermal condition. The controlled hydrolysis of Ti(OⁱPr)₄ in the presence of ionic liquids to form titanium oxo clusters plays a key role in the formation of anatase nanostructures. The more condensed titanium oxo clusters may improve the formation of the nanostructures. Compared to other ionic liquids mediating procedures, our methods have advantages of using less amount of ionic liquids (2 eq.) and ionic liquids can be repeatedly used. **It is worth noting that ionic liquids are normally considered as stable media or as innocent solvent. Our results indicate that not all ionic liquids were stable in the reaction system. Some may lead to reactions playing a prominent role for the formation of TiO₂ nanostructures. The application of TiO₂ nanoparticles in optic coating and the solvothermal reactions of Zr(OPr)₄ in ionic liquids to synthesize ZrO₂ nanoparticles are ongoing in our lab.**

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