This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Exceptional thermal stability of undoped anatase TiO\textsubscript{2} photocatalysts prepared by a solvent-exchange method

Igor Krivtsov,\textsuperscript{a,b} Marina Ilkaeva,\textsuperscript{a,c} Viacheslav Avdin,\textsuperscript{b,c} Zakariae Amghouz,\textsuperscript{d} Sergei A. Khainakov,\textsuperscript{d} José R. García,\textsuperscript{e} Eva Díaz\textsuperscript{e} and Salvador Ordoñez\textsuperscript{e}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

A new solvent-exchange technique to prepare anatase nanoparticles with exceptional thermal stability and photocatalytic activity is described here. The process of preparation is accomplished by using organic solvents to precipitate hydrous titania particles from basic aqueous medium containing titanium peroxo complex. Undoped titanium dioxide formed via solvent exchange method has unprecedented thermal stability against transformation to rutile phase, as opposed to TiO\textsubscript{2} prepared by the commonly method of the gelation of aqueous titanium peroxocomplex. On the basis of X-ray thermodiffraction experiment, it has been established that the thermal treatment at 1000 ºC of the titania prepared by ethanol precipitation contains 100% pure anatase phase. The stabilization of anatase is induced by the high defectiveness of TiO\textsubscript{2} nanostructure, which is evidenced from band-gap energy estimation, PXRD and HRTEM studies. The prepared TiO\textsubscript{2} nanoparticles show an outstanding photocatalytic activity comparable to the commercial Aeroxide P25 photocatalyst in UV-assisted decomposition of methylene blue.

1. Introduction

Despite the large number of alternatives [1], titanium dioxide is considered to be the most appropriate semiconductor photocatalyst, because it is inexpensive, non-toxic and thermally stable according to many comprehensive reviews [2–11]. Anatase, generally considered the most active phase for photocatalytic applications, is a metastable polymorph which usually transforms into stable rutile phase in the temperature range of approximately 500-700 ºC. The development of new methods tailored to prepare anatase with increased thermal stability up to the sintering temperature range is of great importance, not only for photocatalysis, but also in other emerging applications such as self-cleaning and antibacterial ceramic production [12]. There are two general procedures to stabilize anatase: Doping TiO\textsubscript{2} with metal cations [13], fluorine [14], or sulfur [15], and preparation of mixed TiO\textsubscript{2}/M\textsubscript{2}O\textsubscript{3} oxides [16,17]. The most significant drawback of these methods is that the dopants reduce crystallinity of TiO\textsubscript{2}, which increases the recombination rate of electron-hole pairs. However, the preparation of stable undoped anatase is also discussed in the literature. Wu et al [18] found that the anatase phase, prepared from titanium isopropoxide in the presence of tetramethylammonium hydroxide, was stable up to 950 ºC. They attributed the retardation of anatase-to-rutile phase transition to the formation of the rod-like crystals. Similar observation about the effect of crystallite size and morphology on the stability of anatase phase was reported by Mao et al [19]. Li et al [20] showed that the formation of intermediate brookite phase would enhance the stability of anatase at high temperatures. Application of simple alkoxide-based sol-gel procedures using urea or formic acid as modifying agents also led to improved stability of the desired titania polymorph [21,22]. But recently, the emerging class of precursors based on peroxo complexes have been used for metal oxide synthesis [23,24]. Moreover, shape of anatase crystals was successfully controlled via hydrothermal treatment of titanium peroxo complexes [25,26]. Etacheri et al [27] used peroxo titanic acid to prepare visible light active TiO\textsubscript{2} photocatalyst with 100% anatase phase after heat treatment at temperature as high as 900 ºC. Herein, we report a new facile solvent-exchange method for preparing TiO\textsubscript{2} nanoparticles. We have found that titanium peroxo complex is insoluble in ethanol and acetone, as a consequence, hydrous titania suspensions were precipitated using these solvents. The proposed technique does not require utilization of toxic, unstable and volatile alkoxide precursors as well as complex organic structure-directing agents or templates. Thus, it can be considered as an environmentally friendly approach for preparing high performance titania photocatalysts. The prepared TiO\textsubscript{2} nanoparticles exhibit temperatures of anatase-to-rutile phase transformation higher than those previously reported [15,18,21,22,27].

2. Experimental

2.1 Chemicals

Titanium oxysulfate hydrate containing not more than 17% of H\textsubscript{2}SO\textsubscript{4}, as well as 30 wt% hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) water solution were purchased from Aldrich. Ammonium hydroxide 20% water solution, ethanol and acetone (all VWR Chemicals)
were of analytical grade and used as received without additional purification. The commercial photocatalyst Aerioxide P25 (Degussa P25) was purchased from Aldrich. The concentration of titanium oxyxulfate was determined gravimetrically prior to its use in synthesis. Titanium oxyxulfate has been chosen as precursor due to its high stability under ambient conditions, which is not the case for titanium tetrachloride or titanium alkoxides.

2.2 Synthesis

Firstly, titanium hydroxide was precipitated from 25 mL of 0.2 M titanium oxyxulfate solution in sulfuric acid by addition of 3 M NH₃ aqueous solution, the final pH of precipitate was 9.0. Then, it was centrifuged at 7000 rpm and washed with deionized water until a negative reaction for sulfate ions was achieved. The aqueous titanium peroxocomplexes were synthesized by addition of 4 mL of 30 wt% hydrogen peroxide to the precipitates and gradual adjustment of the pH value of the reaction mixture to 9.5 by adding ammonia. Finally, clear bright yellow stable solutions were formed and their volumes were adjusted to 25 mL. The solutions were cooled in an ice bath in order to prevent fast decomposition of H₂O₂, as well as evaporation of ethanol and acetone. The cooled solutions of titanium peroxocomplexes were mixed with equal volumes of ethanol or acetone. The mixed solutions became turbid immediately, because the hydrous titania particles were formed. The obtained suspensions were left for 24 h and then centrifuged at 8000 rpm for 5 min, after that the pale-yellow precipitates were isolated and washed several times with water. For the sake of comparison, the sample prepared in the absence of any organic solvents was also investigated. Because the aqueous solution of titanium peroxocomplex synthesized as mentioned above was stable, it was heated at 50 °C for 2 h in order to induce titanium hydrolysis and precipitation of peroxotitana gel. The samples prepared by (i,ii) isolation of hydrous titania with ethanol or acetone and (iii) gelation of aqueous complex solution were designated as TiEtO, TiAc and TiAQ, respectively. All precipitates were dried at 70 °C for 24 h before subjecting to investigation. Also the samples were thermally treated in a muffle furnace at specific temperatures (500 °C, 800 °C, 900 °C and 1000 °C) with a heating rate of 5 °C·min⁻¹ and left for 30 min at each specific temperature before cooling down.

2.3 Characterization

Powder XRD patterns were registered on a Rigaku Ultima IV diffractometer, using Ni-filtered CuKα radiation source. The PXRD data were refined, where unit cell parameters and anatase phase content were estimated using MAUD software and crystal sizes were calculated by Scherrer equation for anatase (101) reflection. Thermodiffraction analysis was carried out using the X’pert Pananalytical diffractometer for TiEt sample calcined at 400 °C for 2 h prior to measurement. TiEt was heated up to 1000 °C at a heating rate of 5 °C·min⁻¹ and the XRD patterns were collected every 30 min during 5 h at this temperature. A Shimadzu UV-2700 spectrophotometer with integrated sphere attachment was used to obtain diffuse reflectance (DR) spectra of the samples using barium sulfate as a reference. Band gap energy was estimated by Kubelka-Munk method. Bruker Tensor 27 spectrometer was used to collect FTIR spectra. Thermal analysis of the samples was performed using a Shimadzu TG/DTA analyser at a heating rate of 10 °C·min⁻¹ under air flow. SEM images were obtained using a FEI Quanta 200F field emission scanning electron microscope equipped with EDX detector; the samples were gold-coated prior to observation. The EDX analysis confirmed the absence of sulfur in the TiO₂ samples. A Micromeritics ASAP 2020 was used to obtain N₂ adsorption-desorption isotherms at 77 K. Before the experiment, the samples were outgassed under vacuum at 400 °C. Surface area and pore volume were calculated using BET and BJH methods. TEM, HRTEM, selected area electron diffraction (SAED), nanobeam electron diffraction (NBD), and EELS (electron energy loss spectroscopy) studies were performed on a JEOL JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 kV, equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-resolution better than 0.19 nm. The samples for TEM were dispersed in ethanol, sonified and sprayed on a holey carbon film coated copper grid and then allowed to air-dry, finally, Gatan SOLARUS 950 was used before observation.

2.4 Photocatalytic activity test

Synthesized titania materials were tested in the aqueous-phase photocatalytic decomposition of methylene blue (MB) in a stirred batch reactor. For the experiments, 25 mg of each sample previously calcined in air at 500 °C, 800 °C and 1000 °C for 30 min was placed into a quartz reactor. Later, 50 mL of MB aqueous solution (20 mg·L⁻¹) was added to the catalyst. Before irradiation, the suspension was magnetically stirred in the dark until the adsorption equilibrium was reached in 30 min. Afterward, the suspension was exposed to ultraviolet irradiation. The UV-light source was 500 W lamp (Helios Italquartz) having maximum emission at 365 nm and equipped with a water-cooling jacket. The reactor with suspension was positioned at a distance of 50 cm from the lamp, which gives a light intensity of 16 mW·cm⁻². The suspension was constantly stirred during the UV-irradiation and 5 mL aliquots were taken every 30 min during 240 min. The solution was separated from the catalyst using a centrifuge, and the concentration was determined photometrically by the absorbance at 664 nm using a Perkin Elmer Lambda 20 spectrophotometer. After that, the solution, together with the catalyst powder were returned back into the reactor and
irradiation has continued. Photolysis of the MB solution in the absence of catalyst was carried out under the same experimental conditions. It was found that only 1.5 % of MB was decomposed under these conditions.

3. Results and Discussion

All the as-synthesized samples were found to be amorphous (see Supplementary Information, Fig. S1), except TiAq sample that shows a broad peak centered at 2θ=9.2° on the XRD pattern, which was attributed to the ammonia peroxo titanate complex [28]. FTIR spectra (Fig. 1) of the as-prepared samples reveal some differences in the structural features of the precipitates. The most intense band at 1385 cm⁻¹ confirms the presence of ammonia in all the samples. The intense and well-defined band at 900 cm⁻¹, observed in the spectrum of the peroxotitanate gel (TiAq), corresponds to the stretching O–O vibrations, while the peak at 696 cm⁻¹ indicates the presence of Ti–O–O bonds. However, the bands corresponding to the peroxo groups are not clearly seen in TiAc and TiEt spectra. A similar observation was made by Liao et al [26], when the solvothermal method is applied to synthesize TiO₂ from the mixture of peroxo titanate complex and organic solvent. We suppose that the reaction between organic solvents and peroxo groups has caused the decomposition of the latter, which in turn, led to the oxolation of hydrous titania species. The broad absorption band centered at 616 cm⁻¹ in TiAc and TiEt spectra is attributed to Ti–O–Ti stretching vibrations, this is most likely due to the very high degree of condensation of oxo-species in these precipitates. Likewise, the decomposition of peroxo groups while preparing the TiAc and TiEt samples is also evidenced by DR-UV-vis spectroscopy study (Fig. S2). The TiAq sample absorbs light in the visible region due to the presence of peroxo groups on titania. Contrarily, the visible light absorbance is considerably decreased in the case of the TiAc and TiEt samples (Fig. S2). Moreover, this method provides additional information about structural features of titania particles and coordination state of titanium. The sharp absorption peak at 219 nm in TiAq spectrum can be attributed to the charge transfer process in isolated TiO₂ units [29]. The shifting of absorbance bands towards longer wavelengths indicates the presence of large titania particles. The absorbance bands at 334 nm in the TiEt and TiAc spectra suggest that these samples show more condensed TiO₂ phase compared to the TiAq sample. Thermal analysis of the as-synthesized samples was carried out in order to determine the temperatures for the elimination of volatile components and exothermic effects associated with phase transitions. Thermal decomposition of the TiAq is similar to that one reported previously [28]. The DTG curve shows one endothermic and three well-defined exothermic peaks corresponding to the elimination of adsorbed and chemically bonded water, decomposition of peroxo groups and crystallization process of amorphous titania (Fig. S3a). However, thermal decomposition of the TiAc and TiEt samples prepared via solvent-exchange method is different (Fig. S3b,c). Similarly to TiAq sample, there are three exothermic peaks on the DTG curves for TiAc and TiEt, but unlike the TiAq sample, the first two exothermic peaks observed at low temperature correspond to the combustion process of the organic residue. The as-prepared samples start to crystallize around 300 °C and with further heat treatment their crystallinity increases (Fig. 2). The results of XRD analysis are summarized in Table 1. Titania sample TiAq prepared from the aqueous peroxotitanate gel has the lowest thermal stability among all samples, however, its stability is much higher than TiO₂ prepared via conventional non- peroxo techniques [27]. Rutile phase is detected in the TiAq sample after treatment at 900 °C.
and the complete anatase-to-rutile transition takes place at 1000 °C. The TiAc sample is more stable, it contains pure anatase phase after being subjected to 900 °C for 30 min. Furthermore, titania prepared by solvent-exchange method using ethanol (TiEt) shows a remarkably higher stability, it retains 96 wt% of anatase phase even after heat treatment in muffle furnace at temperature as high as 1000 °C. In order to investigate the process of anatase-to-rutile transformation in-situ, X-ray thermodiffraction study was performed for TiEt sample (Fig. 3a). It shows that the TiEt sample possesses unprecedented stability towards formation of rutile phase, it retains 60 wt% of anatase phase after being treated at 1000 °C for 5 h (Fig. 3b). The slight controversy observed in the percentage of rutile phase, when TiEt sample is thermally treated in muffle furnace or during the thermodiffraction experiment, is attributed to overheating of the sample in the furnace, which leads to the formation of 4% of rutile phase after 30 min, while 150 min in the diffractometer heating chamber was necessary to reach the same percentage of transformation. According to XRD data, we cannot attribute the hindering of anatase-to-rutile phase transformation to the crystallite size effect, because the differences in this parameter are insignificant. The differences in the c-axis lattice parameter indicate that crystalline anatase formed from TiAc and TiEt precursors contains higher concentration of defects than that prepared from TiAq one. The above hypothesis is corroborated by the results of band-gap (BG) energy estimation (Table 1). Usually BG energy of anatase TiO₂ is 3.2 eV, however, this value varies depending on the presence of dopants and degree of crystallinity. Like Etacheri et al [27], we observe the band gap shrinkage when TiO₂ anatase is prepared via aqueous titanium peroxocomplex route (TiAq). It can be attributed to the nitrogen-doping effect in the samples calcined not higher than 500 °C, as the presence of nitrogen is evident from the EELS data (Fig. S4). After thermal treatment at 800 °C its BG value increases, but it is still less than 3.2 eV, due to the presence of oxygen vacancies formed on sites of the removed N atoms (Table 1). However, TiAc and TiEt samples obtained by solvent-exchange route show broader BG, even though nitrogen-doping occurring when they are treated at 500 °C, and then no nitrogen is detected at calcination temperatures higher than 800 °C (Fig. S4). This indicates high concentration of defects in the structure, and it also means that nitrogen-doping could play some noticeable role, but cannot be solely responsible for the defects formation at elevated temperatures. The formation of defects is likely to be due to rapid loss of ligands, i.e. peroxy groups, which are not stable in organic solvents. This leads to fast assembling process of the oxide network. On the contrary, the aqueous peroxotitanate gel containing peroxy groups is stable up to high temperatures [30], and because peroxy groups hinder the condensation of titania species, the crystallization rate becomes slow. As a result, less defective structure is formed. TEM and HRTEM images and electron diffraction (ED) patterns of pure anatase TiAq and TiEt samples calcined at 800 °C are shown in Figs. 4 and 5. Both samples show the presence of crystal grains with the average size of ca. 45 nm and 50 nm for TiEt and TiAq (Fig. 4a-d, Fig. S5), respectively, in agreement with the results obtained from XRD analysis. From a careful inspection of SAED patterns (Fig. 4e,f) and NBD patterns for individual crystal grains (Fig. 4g,h), the degree of crystallinity seems to be similar for both samples and all ED patterns have been indexed as anatase phase. No detectable traces of rutile phase have been found by indexing the ED patterns. TEM images reveal mesoporous crystal grains with pore diameters in the range 3-12 nm in the case of TiEt sample (Fig. 5a). HRTEM images displayed in Fig. 5c-f for both

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>Unit cell parameters (Å)</th>
<th>Crystal size (nm)</th>
<th>Anatase: Rutile ratio (%)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
<td>Anatase</td>
<td>Rutile</td>
</tr>
<tr>
<td>TiAq</td>
<td>500</td>
<td>3.785(4)</td>
<td>9.508(4)</td>
<td>22</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>3.782(2)</td>
<td>9.525(2)</td>
<td>49</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.783(1)</td>
<td>9.534(1)</td>
<td>49</td>
<td>100:0</td>
</tr>
<tr>
<td>TiAc</td>
<td>500</td>
<td>3.785(2)</td>
<td>9.507(4)</td>
<td>29</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>3.785(2)</td>
<td>9.516(1)</td>
<td>41</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.785(4)</td>
<td>9.518(1)</td>
<td>52</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.782(1)</td>
<td>9.517(1)</td>
<td>64</td>
<td>96:4</td>
</tr>
<tr>
<td>TiEt</td>
<td>500</td>
<td>3.784(4)</td>
<td>9.503(4)</td>
<td>31</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>3.784(4)</td>
<td>9.509(2)</td>
<td>44</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.784(1)</td>
<td>9.513(1)</td>
<td>48</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.783(1)</td>
<td>9.516(2)</td>
<td>76</td>
<td>96:4</td>
</tr>
</tbody>
</table>
Fig. 4 (a-d) TEM images, (e,f) selected area electron diffraction (SAED) and (g,h) nanobeam electron diffraction (NBD) for the TiEt (left) and TiAq (right) thermally treated at 800 ºC samples show an interplanar spacing of 0.35 nm corresponding to (101) atomic planes. Several line defects, such as dislocations, along the (101) plane have been observed in the case of TiEt (Fig. 5c,e), while very distinguishable planar defects, such as grain boundaries, are manifested in the case of TiAq (Fig. 5b,f).

Obviously, the blurred lattice fringes observed in HRTEM images in the case of TiEt, such as Fig. 5c, are an indication of the defects induced from the lattice distortion, probably attributed to the crystallization process. EELS spectra for TiAq and TiEt, are shown in Fig. S6. Because of the octahedral coordination of Ti atoms, the L3 and L2 edges are then both subdivided into two edges by the strong crystal-field splitting arising from the surrounding O atoms [31]. The splitting of Ti L2,3 edges slightly higher in the TiAq, which may reflect that the local octahedral coordination is weakly present in the case of the TiEt, probably due to the degree of crystallinity and/or the structural defects as confirmed by HRTEM study. The splitting of O-K edge with a separation of 2.4 eV for TiAq and TiEt (Fig. S6) confirms the anatase phase [32]. TEM and SEM images of TiAq calcined at 800 ºC (Fig. 4b,d and Fig. S7a) show the presence of sintered oxide composed of large densely packed grains, while the images of TiEt (Fig. 4a,c and Fig. S7c) show unagglomerated TiO₂ grains and with the increase of calcination temperature leads to the formation of densely packed large particles (Fig. S7d).

The TiEt sample exhibit high photocatalytic activity for the decomposition of MB when compared to the TiAc and TiAq samples calcined at 500 ºC (Fig. S8). The crystallinity of TiO₂ is improved after calcination at higher temperatures (Table 1), this fact may lead to enhancement of photocatalytic activity. Despite the crystallinity of the TiAq sample is improved by thermal treatment at 800 ºC, this sample does not show any increase of photocatalytic activity, which is probably attributed to its densification and therefore resulting in low BET surface area of just 9 m²g⁻¹ (Fig. S9). However, the TiEt sample treated at the same temperature retains higher surface area (34 m²g⁻¹) and mesopore volume (Fig. S10). The decomposition rates of MB
the presence of TiEt or TiAc samples calcined at 800 °C reach almost the values obtained by the commercial photocatalyst Aerioxide P25 (Fig. 6a). This known commercial photocatalyst has proved to be very efficient; however it shows poor thermal stability compared to the TiEt and TiAc samples. The calcination of Aerioxide P25 at temperatures higher than 800 °C induced the full transition from anatase phase to the photocatalytically less-active rutile phase (Fig. S11). Obviously, 100 % pure anatase phase up to 900 °C, high surface area and mesoporosity of the TiEt and TiAc samples are the main contributors to the outstanding photocatalytic activity (Fig. 6a). When TiEt and TiAc are thermally treated at 1000 °C, their photodecomposition rate of MB decreases. However, their photocatalytic activity is still nearly twice higher than for Aerioxide P25 treated at the same temperature (Fig. 6b). Moreover, the degree of MB photodegradation in TiAc sample was slightly enhanced compared to the TiEt, which could be attributed to the better charge separation on the anatase-rutile interface [33,34].

Conclusion

In summary, we have developed and described a new solvent-exchange method for the preparation of undoped TiO₂ photocatalysts with unprecedented anatase thermal stability and outstanding photocatalytic activity. We have succeeded in preparing mesoporous pure anatase TiO₂ nanoparticles which are stable up to 1000 °C. The preparation procedure is completed by using ethanol to precipitate hydrous titania particles from basic medium containing titanium peroxo complex. High thermal stability against anatase-to-rutile phase transformation is caused by the defectiveness of the formed TiO₂ structure, which is the consequence of the rapid decomposition of titania peroxo species. The photocatalytic activity of the prepared TiO₂ materials, thermally treated at temperatures higher than 800 °C, is superior to the commercial Aerioxide P25 photocatalyst treated at the same conditions. The thermal stability of anatase up to the sintering temperatures, along with its high photocatalytic activity, offer new possibilities to prepare a wide range of self-cleaning and anti-bacterial TiO₂-based ceramic materials to meet medical and domestic needs.

Acknowledgement

We gratefully acknowledge financial support from the Spanish MINECO (MAT2013-40950-R, CTQ2011-29272-C04-02, and Técnicas de Infraestructuras Científico-Tecnológicas grants PTA2011-4903-I to Z.A. and PTA2011-4950-I to S.A.K.), the Government of the Principality of Asturias (Severo Ochoa PhD grant BP-14-029 to M. I.) and FEDER. South Ural State University acknowledges financial support of The Ministry of Education and Science of the Russian Federation Grant No 16.2674.2014/K.

Notes and references

1 A. Name, B. Name and C. Name, Journal Title, 2000, 35, 3523; A. Name, B. Name and C. Name, Journal Title, 2000, 35, 3523.
RSC Advances Accepted Manuscript

Page 7 of 8

Page 7 of 8

This journal is © The Royal Society of Chemistry [year]
Table of Content
A new solvent-exchange method for preparation of undoped anatase TiO$_2$ nanoparticles with unprecedented thermal stability has been presented.