Easy and Fast Preparation of TiO₂-based Nanostructures Using Microwave Assisted Hydrothermal Synthesis

Bruna Andressa Bregadiolli*, Silvia Leticia Fernandes*, Carlos Frederico de Oliveira Graeff*  

* POSMAT, Universidade Estadual Paulista “Júlio de Mesquita Filho”, Av. Eng. Luiz Edmundo C. Coube 14-01, 17033-360, Bauru, SP, Brazil  

b Instituto de Química de Araraquara, Universidade Estadual Paulista “Júlio de Mesquita Filho” Prof. Francisco Degni 55, 14800-060, Araraquara, SP, Brazil  
c Departamento de Física, Universidade Estadual Paulista “Júlio de Mesquita Filho”, Av. Eng. Luiz Edmundo C. Coube 14-01, 17033-360, Bauru, SP, Brazil  

Received: September 17, 2016; Revised: February 22, 2017; Accepted: March 10, 2017  

TiO₂ derivatives with distinct morphologies have been successfully obtained by microwave assisted hydrothermal synthesis in acidic and alkaline medium using mild conditions. Titanium tetraisopropoxide (TTIP) was used as precursor in different environmental conditions under low temperatures, inferior to 150 °C, and short synthesis times, from 2 to 60 min. X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N₂ adsorption at 77 K (BET) were used to characterize the microstructural properties of the oxides. In the acidic synthesis the reaction time and temperature are not accompanied by significant changes in the structure of the material. However, in the basic conditions, the concentration of Na⁺ ions strongly influences the particle morphology and growth. The morphology of the nanoparticles shows irregular spheres in acidic conditions, while in alkaline medium, needle like structures are formed as well as aggregated nanotube-like structures synthesized in only 30 min. Besides the difference in the morphology and structure, in both systems, high surface area was obtained.  

Keywords: nanostructures, titanium dioxide, microwave assisted hydrothermal synthesis, crystal growth

1. Introduction  

Nanocrystalline titania (TiO₂) has been intensively investigated due to its numerous applications in many fields such as photocatalysis, photovoltaic cells and gas sensors. It is cheap, abundant, chemically stable and a multi-functional material. There are three natural polymorphs of TiO₂: rutile, brookite and anatase. Anatase has a low electron hole recombination rate and due to its high photoactivity is believed to be the most favorable phase for solar energy conversion and photocatalysis. It is an n-type semiconductor with an indirect band gap of 3.2 eV. Particle size has great influence on the structure and properties of TiO₂. In the nanometric regime, anatase is the most stable polymorph. For example in dye sensitized solar cells (DSSC), small particle sizes are desired since greater surface area increases the contact of the nanoparticles with the dye and thus optimizes charge transfer and decreases charge recombination.  

For each application, careful tailoring of specific properties such as phase composition, surface area and morphology is requested. So, several TiO₂ nanostructures such as spheres, nanorods and nanotubes have been synthesized using different techniques including sol-gel, electrochemical, sonochemical and hydrothermal. Hydrothermal synthesis is an environmentally friendly methodology used to synthesize nanostructured materials. The starting material, synthesis conditions and processing can drastically change the final product. For example, Kim et al. obtained well-defined spherical mesoporous TiO₂ prepared from titanium tetraisopropoxide (TTIP). Kasuga et al. have obtained titanates nanotubes from TiO₂ nanopowder with high concentrations of NaOH. The hydrothermal synthesis is typically done using an autoclave with Teflon liners under controlled temperature and/or pressure in aqueous solutions. Despite its advantages, the synthesis can take several hours to be completed. Microwave assisted approach has been used to synthesize many classes of materials such as oxides and hybrid materials. This technique provides uniform distribution of energy inside the sample, better reproducibility and excellent control over experimental parameters. Microwave reactions were found to reduce the hydrothermal synthesis time of TiO₂ by typically 1/3, and in addition can produce single crystals, with less waste and lower temperatures. TTIP is commonly used in conventional and microwave assisted hydrothermal synthesis of TiO₂ under acid conditions, but less in alkaline. Most of the titanate nanotubes synthesis using microwave have TiO₂ nanopowders as precursor, as a consequence, higher temperatures and times are needed. Wu et al. synthesized multiwall structured titanate nanotubes from powders at high NaOH concentration (8–12 M) for 90 min.
Also, Ou et al.\textsuperscript{10} obtained nanotubes with surface area of 256 m\textsuperscript{2}/g synthesized at 130 °C for 90 min.

In this work, we present an easy and fast route for TiO\textsubscript{2} nanostructures synthesis using microwave assisted hydrothermal technique in alkaline and acidic mediums. We demonstrate an environmentally friendly synthesis that uses mild conditions, fast reaction times and low temperatures and gives nanoparticles with different morphologies, high yield and surface area. We have obtained titanate needle like particles after 30 min of synthesis using TTIP in alkaline medium. The facility in producing these nanostructures, its reproducibility and low cost make it attractive for industrial applications.

2. Experimental

Titanium tetraisopropoxide (TTIP) (Alfa-Aesar 97\%), HNO\textsubscript{3} (Dinâmica) and NaOH (Synth) were used as received. For the acidic synthesis, 12 mL (0.4 mol) of TTIP was added dropwise in a 0.01 M HNO\textsubscript{3} solution. For the alkalyne synthesis, 12 mL (0.4 mol) of TTIP was added dropwise in NaOH solutions with different concentrations: 0.1, 1 and 10 M. The solution volume used was fixed at 40 mL in a 100 mL autoclave. In both cases, the precursor solution was stirred for 6 h at 80 °C. The solution was poured into a Teflon autoclave placed inside a modified domestic microwave oven (Panasonic Piccolo 800 W) coupled with an external temperature controller (Incon CNT120). The pressure of the system was not externally controlled and reached a maximum of 10 bar. The synthesis temperature varied from 110 to 150 °C and the synthesis time from 2 to 60 min. Subsequent to the synthesis, the colloidal solution was washed with water. Notice that the alkaline synthesis at 10 M (sample HMB150-30-10) was washed with HCl 0.1 M in order to remove the remaining Na\textsuperscript{+} ions.\textsuperscript{13} The solutions were centrifuged at 2500 rpm and dried in an oven at 60 °C. The samples were named as follow: HM (for the acidic medium) or HMB (for the alkaline medium), followed by the temperature and synthesis time. For the HMB samples, in addition the NaOH concentration is presented. Details about the synthesis parameters used are presented in the Supplementary Material, Table S1. X-ray diffraction (XRD) was done in a Rigaku RINT2000 diffractometer with CuK\textalpha\ radiation, using 40 kV and 20 mA. Scanning electron microscopies (SEM) were performed using a FEI Inspect F50 and a Philips XL30-FEG. The size of the nanoparticles was measured using transmission electron microscopy (TEM) using a Philips CM120 and 200 kV. The surface area and pore size were determined by Brunauer–Emmett–Teller (BET) adsorption of nitrogen at 77K in a Micromeritics ASAP 2010. The surface area was calculated from the adsorption isotherm.

3. Results and discussion

3.1 Acidic medium

Table S1 summarizes the results of the acidic medium synthesis as the morphology and the yield for all times and temperatures used. The temperatures were chosen above the boiling point of water to reach the solvent vapor pressure saturation.

Figure 1 shows the XRD pattern of a sample synthesized at 110 °C for 5 min. The patterns exhibits the predominance of the anatase phase (JCPDS 21-1272). However, a diffraction at \(2\theta = 31.8°\) (* in the Figure 1) attributed to the (211) plane of the brookite phase (JCPDS 29-1360) is observed. It is known that brookite phase can be formed in hydrothermal synthesis in high temperatures and pressure.\textsuperscript{28} Also a peak of rutile phase can be observed (# in the Figure 1).\textsuperscript{29} The diffractions patterns for all HM samples are similar, see Supplementary Material, Figure S1.

The crystallites size was estimated using the Scherrer equation\textsuperscript{30} and it was found to be close to 6.0 nm for all materials analysed; for this purpose the most intense peak at \(2\theta = 25.49°\) \# was used, see Table S2 in the Supplementary Material. The intensity of the diffraction peak is correlated to the volume of the phase and crystallite size. For very small crystallites, the peaks are broad as can be seen in Figure 1.

No clear dependence on the particle size or its morphology was observed according with the synthesis parameters used, as observed in SEM and TEM images, Figure 2 and 3. Analyzing the images, it is possible to note that the particles are agglomerated. Aggregation is expected due to the presence of a Ti(OH)\textsubscript{4} amorphous phase, due to the lack of a sintering step. In Figure 2, SEM images of HM110-15 and HM150-60 are presented, for other samples see Figure S2 in the Supplementary Material.

On the order hand, analyzing the TEM images, Figure 3a and 3b, it is possible to observe that the nanoparticles have sizes between 10 and 15 nm (sample HM150-30), which was confirmed from the size distribution study, made using ImageJ software presented in Figure S3. The Selected Area
Figure 2: SEM images of samples prepared at a) HM110-15 and, b) HM150-60.

Figure 3: TEM images obtained with different magnifications (a) and (b), Electron Diffraction Pattern (c) and BET adsorption curve (d) for sample HM150-30.

Electron Diffraction Pattern (SAED) in Figure 3c shows in agreement with the X-ray diffraction that the samples are predominantly crystalline. The surface area from BET for this sample is 207 m²/g. The adsorption curve shown in Figure 3d is typical for a microporous material with relatively small external surface.

In summary, the synthesis parameter used do not affect the morphology, crystallite size and crystalline phase however, they do influence the nanoparticles synthesis yield. For short times, 2 and 5 minutes, the yield obtained were lower than 30% even at the highest temperature. Whereas the synthesis yields at 150 °C and 30 min was 93%. For the yield determination, each reaction was repeated at least 3 times and the yields presented in Table S1 are the average values found.

The best yields were obtained for synthesis from 30 to 60 min at 150 °C. In order to understand the different yields observed and the small dependence of the nanoparticles obtained on synthesis parameters, we shall start discussing the nanoparticles synthesis reaction. The precursor solution is formed with the loss of the organic groups from TTIP and hydrolysis, which leads to the formation of Ti(OH)₄(OCHCH₃)₆-x species. The hydrolysis reaction of titanium alkoxide is a fast process and dominates the morphology and final particle size, for that reason the precursor solution was slowly dropped into water and kept under vigorous stirring at 80 °C when a whitish transparent solution was obtained. In the second step, the addition of HNO₃ acts as a peptizing agent forming crystallites with low crystallinity by hydrolysis. In aqueous medium, protonated surfaces of TiO₆ octahedra easily combine with hydroxyl groups of other TiO₆ octahedra to form Ti–O–Ti bonds by water elimination, resulting in amorphous nanoparticles. The use of microwave hydrothermal
processing of colloidal TiO$_2$ solutions allows rapid heating, fast kinetics of crystallization and formation of a large number of clusters that grows from amorphous nanoparticles and assemble into TiO$_2$ nanocrystallite aggregates.\(^{36}\) This reaction is characterized by the formation of a high concentration of aggregated nanoparticles. Additionally, it is known that the size of the particle and additional conditions such as surface stress/strain influence the crystalline phase.\(^{37-39}\) In general, anatase is the most stable crystalline phase for particles smaller than 11 nm, brookite for particles between 11 and 35 nm and rutile for particles bigger than 35 nm.\(^{40}\) In this way, our results indicate that the fast cluster formation, due to the microwave heating, is responsible for the small crystallites and nanoparticles obtained as well as its aggregation. The crystalline materials formed exhibits the predominance of the anatase phase with some brookite nanoparticles formed due to the pressures inside the autoclave. Normally the simplest way to control the crystal size is by microwave synthesis time. However, in our results there is no clear difference in the size of the nanoparticles depending on time. The crystal growth mechanism observed is compatible to an oriented aggregation of small primary subunits.\(^{41}\) We observed the highest yields for the highest temperature and times higher than 30 min. Thus, it is assumed that in this system, 30 min is the minimum synthesis time for the nucleation and growth of the nanoparticles. For times higher than 30 min no difference in yield is observed which can be attributed to the Ostwald ripening process, in which the particles re-dissolve after a critical time, thus the yield is basically time independent after this time.\(^{42}\) Notice that in microwave hydrothermal synthesis high internal surface areas are expected,\(^{43}\) in our case 207 m$^2$/g.

### 3.2 Alkaline medium

Similarly, the syntheses under alkaline environments were performed in different conditions. The temperature was 110, 130 and 150 °C, using 5, 15, 30 and 60 min of treatment time for the concentration of 1 and 10 M NaOH.

We shall start with the effect of the synthesis time in the 1M precursor solution. The XRD patterns for these samples are presented in Figure 4 (see also Figure S4 for 110, 130 and 150 °C). The diffraction patterns are similar for all the synthetic conditions. They have shown a preferred orientation in the direction of the peak at 2θ = 48.1 ° which can be attributed to Na$_2$Ti$_6$O$_{13}$ (JCPDS 73-1398).\(^{32}\) Analogous to the acidic system, the synthesis time did not influence the crystalline phase and morphology. However, the time influences the yield of the synthesis and the optimum yield, > 90 %, was obtained after 30 min of synthesis.

The influence of Na$^+$ in the crystal growth was addressed using different NaOH concentrations during the synthesis. In Figure 5 the XRD patterns for the powders prepared using 10 M (HMB150-30-10) and 0.1 M (HMB150-30-0.1) are shown. It can be seen that the sample with the highest concentration of NaOH follows the same diffraction pattern of the titanates, in this case Na$_2$Ti$_3$O$_7$ (JCPDS 31-1329).\(^{33}\) The lower concentration shows the anatase phase, similarly to Figure 1. Notice that the peak of the brookite phase in 2θ = 31 ° is observed for the sample HMB150-30-0.1. From SEM images, Figure 6, it was possible to observe that the samples with low concentration of NaOH and the samples synthesized in acidic medium (Figure 2 and 6a) present similar morphology and the samples synthesized using 10 M NaOH (Figure 6b) present morphology dominated by needle-like structures. The SEM image of the samples HMB150-30-1(Figure 6c) presents a mixture of needle like structures and irregular spheres as observed in lower concentrations of NaOH.

The BET adsorption curve, Figure 6d, shows a steep increase in the isotherm, followed by a plateau which indicates a microporous material with relatively small external surface. The plateau is reached as soon as the surface is completely covered.\(^{34}\) Due the difference on the morphology of the nanoparticles synthesized in acid and alkaline medium, the surface area value of the sample HMB150-30-10 obtained by BET is high, 375 m$^2$/g.
Figure 6: SEM images for the samples a) HMB150-30-0.1, b) HMB150-30-10, c) HMB150-30-1 and d) HMB150-30-10 BET adsorption curve.

The SEM images of the samples synthesized at 110 °C present sphere-like aggregated that are composed by nanosheets, observed in higher magnifications, Figure S6a and Figure S6b. The samples synthesized at 130 °C presented a mixture of nanocables and nanoparticles, and the same trend of nanosheets observed in lower temperature of treatment, Figure S6c, Figure S6d and Figure S6e. The sample synthesized at 150 °C present a mixture of needle like structures and irregular spheres as observed in lower concentrations of NaOH, Figure S6f, Figure S6g and Figure S6h. It is important to note that the same trend of morphologies were observed in the various temperatures, however, the samples treated at 5 min, presented the most heterogeneous and bigger nanoparticles, Figure S6g.

TEM image of the sample HMB150-30-10 after HCl washing is shown in Figure 7a. It is possible to observe aggregated nanotube-like structures. Na⁺ ions are detected by EDX in both samples, as synthesized and after washing, as presented in Figure 7b and 7c. However, the sample after washing, Figure 7c, has the peak attributed to Na⁺ ions decreased to 0.2 of initial value, suggesting that the Na⁺ ions are removed by HCl washing. The peaks of Si are coming from the substrate used for the EDX measurements.

In the hydrothermal synthesis the morphology and phase formation are more related with the pressure and temperature inside the reactor during the polycondensation step. The TiO₂ formation is weakly affected by the additive, HNO₃ or NaOH when it is close to the neutral condition, i.e. 0.01 M HNO₃ and 0.1 M NaOH, which explains the higher crystallinity for HMB150-30-0.1 compared to HMB150-30-10. On the other hand, at high NaOH concentrations, 1 M and 10 M, remarkable differences were observed, needle-like titanates were synthesized, probably due to the influence of Na⁺ ions on the formation of the crystalline structure.

In the literature few works are dedicated to investigate the influence of acidic and alkaline environments using TTIP as precursor on the nanoparticles formation. Zhao et al. have study the influence of the NaOH and HCl on the formation of nanostructures with different crystalline phase and morphologies using hydrothermal synthesis and tetrabutyl titanate as precursor. They obtained analogous materials as we did, i.e. anatase with brookite for the lowest concentrations of additives, or in conditions closest to neutral. For high NaOH concentrations, they obtained titanate nanoribbons. The difference between our material morphology and theirs can be attributed to the precursor used and synthesis technique. The ability of microwaves to influence the dissolution rate of various precursors (due to different dielectric properties) strongly affects the nucleation and crystallization rates. The organic species undergo chemical
Easy and Fast Preparation of TiO₂-based Nanostructures Using Microwave Assisted Hydrothermal Synthesis

Reactions that are responsible for supplying the “monomers” for nucleation and growth of the inorganic nanoparticles, which can be related to the pronounced shape anisotropy observed in Figure 5. In this way, the reaction proposed for the formation of the needle-like structures is based on the most accepted mechanism for nanotubes formation starting from TiO₂ spherical nanoparticles. Ti – O – Ti bonds are broken by NaOH to create an intermediate containing Ti – O – Na and Ti – OH bonds, which grows in preferential directions. Instead, in our case the hydrolyses of TTIP directly on the solution forms intermediates that have the format of sheets due to the interaction of the TiO layers with Na⁺ and H⁺. The growth generates layered titanate structure with intercalated Na⁺ ions. As shown in Figure 7b and 7c, some of the Na⁺ ions can be removed by HCl rinsing. Here, we have obtained aggregated nanotube-like structures in 30 min of treatment using TTIP as precursor with high surface areas, of 375 m²/g.

From the point of view of applications, Dar et al. obtained anatase nanostructures ~ 7 nm using microwave solvothermal technique using titanium thiobenzoate complexes as precursor at 200 °C and fabricated from this materials DSSC with efficiencies of 6.5%. Shen and coworkers, used also TTIP as precursor, and did their synthesis at 220 °C for 30 min. They obtained anatase nanoparticles with ~ 20 nm in diameter and surface area of 152 m²/g which were used in DSSC with conversion efficiency of 7.8%. Thus our results indicate that the synthesized nanoparticles with up to 375 m²/g of surface area have great potential in DSSC.

4. Conclusions

Nanostructured titanium oxide was successfully synthesized by the microwave assisted hydrothermal technique. The nanoparticles were obtained at mild conditions using low temperatures and short synthesis times, as low as 2 minutes. The XRD patterns show that the TiO₂ nanocrystals are predominantly in the anatase crystal phase though brookite crystalites are also present. The crystallite sizes in acidic solutions have 5 to 6 nm in diameter and aggregate into particles of 15 nm. The reaction time and temperature do not change significantly the structure of the material. In the presence of high concentration of NaOH the morphology and phase are changed to titanates nanotube-like structures, obtained after 30 min of synthesis. The structures obtained, that resemble needles, have the crystalline phase of Na₅Ti₆O₁₃ and Na₂Ti₃O₇. For lower NaOH concentrations aggregated nanoparticles were obtained similar to the ones obtained using HNO₃ as peptizing agent. In both systems, high surface areas were obtained which indicates that these materials are suited for photovoltaics or catalysis.

5. Acknowledgements

The authors would like to thank the financial support of FAPESP (2011/02205-3), CEPID-FAPESP (2013/07296-2), INCT, CNPq and CAPES.

6. References


919


**Supplementary material**

The following online material is available for this article: Structural information of the surfaces