

PCCP

Accepted Manuscript



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. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it 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.

SIMPLE AQUEOUS ELECTROCHEMICAL METHOD TO SYNTHESIZE TiO₂ NANOPARTICLES

Ivan Bezares¹, Adolfo del Campo², Pilar Herrasti¹, Alexandra Muñoz-Bonilla¹

¹Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, C/Francisco Tomás y Valiente, 7, Cantoblanco, 28049 Madrid, Spain.

²Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, Madrid 28049, Spain.

Abstract

Here, a simple and rapid electrochemical approach to synthesize TiO₂ nanoparticles in aqueous solution is reported. This method consists in the electro-oxidation of titanium foil in a tetrabutylammonium bromide aqueous solution, which acts as both electrolyte and surfactant. Amorphous TiO₂ particles in the nanoscale (~5 nm), well dispersed in aqueous solution, were directly formed by applied low current densities in short reaction time. It was demonstrated that several experimental parameters influence the reaction yield; an increase in the current, temperature and reaction time augments the quantity of the obtained material. Then, the amorphous nanoparticles were completely crystallized into pure anatase phase by thermal treatment under air atmosphere as analyzed by X-ray diffraction and Raman spectroscopy. Besides, the size of the nanoparticles increased to approximately 12 nm in the calcination process. The band gap energies of the resulting TiO₂ anatase nanoparticles were determined by diffuse reflectance measurements according to the Kubelka Munk theory, revealing low values between 2.95 to 3.10 eV. Therefore, results indicate the success of this method to create TiO₂ nanoparticles in aqueous medium with good optical properties.

Introduction

Titanium dioxide (TiO_2) is a fascinating material, which started to use in photoelectrochemical solar energy conversion in the early 60s and has been employed in other traditional and emerging areas such as cosmetics, sunscreens, environmental photocatalysis, self-cleaning surfaces, antifogging and antimicrobial systems, among others^{1,2,3}. This broad field of application and the exponential growth of research interest in these materials and nanomaterials come from its excellent properties of high stability, biocompatibility and semiconductor characteristics capable of generating charge carriers by absorbing photon energies. All these structural, thermal, optical and electronic properties are highly dependent on the size, shape, presence of dopants, defect content and phase of the nanostructures. Thus, the well-controlled synthesis of precise nanostructures is crucial to impart the desired characteristic of the final material and in this sense the synthesis method determines, in a large extend, those properties. Many procedures have been used to prepare TiO_2 nanoparticles⁴ including chemical and physical methods. Larger quantity of materials is typically produced by physical methods; however, a better control of the size, shape and composition is achieved by chemical strategies. In particular, solution methods are probably the most employed due to the fine control of the nanoparticles, and especially interesting are those in aqueous medium. These last strategies basically consist in two main steps, hydrolysis and condensation. The sol-gel method, probably one of the most employed in aqueous solution is based on the acid catalyzed hydrolysis of titanium precursors such as alkoxide or chloride followed by condensation^{5,6}. However, although new developments have improve this process⁷, usually the method encounters some problems mainly because the reactions are too fast and the control over the size and dispersibility is poor. Besides, this process normally results in amorphous or poorly crystalline particles;

thereby a posterior thermal treatment is needed. Another common method to produce nanoparticles of TiO_2 is the hydrothermal process from precursor such as TiCl_4 in aqueous solution⁸, conducted under controlled pressure and temperature. In this method the crystallinity of the resulting nanoparticles is considerably improved, strongly influenced by the starting materials and experimental conditions⁹. The drawbacks of this method include the requirement of a high-pressure vessel, high temperature and a relatively long processing time. Besides these common methodologies in aqueous solution to synthesize TiO_2 nanoparticles, electrochemical process in aqueous media has been extensively used to create nanostructures on surfaces, mainly nanotubes¹⁰. The strategies are based on the formation of TiO_2 layer on the surface of Ti foil electrode by electrochemical anodization in acidic solution¹¹. Titania nanoparticles have been also formed and deposited onto surfaces via electrochemical, concretely by cathodic electrodeposition of a Ti hydroxide thin film from an acidic aqueous solution^{12,13}. Inspired in those electrochemical methods, Tang *et al.*¹⁴ developed a novel one-pot approach to produce TiO_2 microparticles and highly porous titanate micro-spherulite particles via simultaneous electrochemical anodization and spark discharge of the anodized oxide layer into an aqueous solution.

Herein we develop a new electrochemical approach to synthesize TiO_2 nanoparticles in aqueous solution, which consists in the galvanostatic electro-oxidation of a titanium foil by applying low current density. In this strategy tetrabutylammonium bromide is used as electrolyte and at the same time acts as surfactant to avoid agglomeration of the resulting nanoparticles. The influence of experimental parameters such as current densities, temperature and reaction time on the electrochemical process was also investigated. The crystalline phase after a thermal treatment and their band gap energies

were thoroughly studied to evaluate the potential of the TiO₂ nanoparticles obtained by this approach.

Experimental section

Synthesis of TiO₂ nanoparticles

Titanium oxide nanoparticles were prepared via electrochemical route in aqueous media at low temperatures. Foils of titanium (99.7%, Aldrich) were used as anode (2 cm² of effective area) and cathode (4 cm² of effective area). The electrodes were placed parallel to each other, and were immersed in 100 mL of a tetrabutylammonium bromide (99%, Across organics) (40 mM) aqueous solution. This electrolyte also acts as surfactant to avoid agglomeration. Subsequently, different currents were applied to the cathode and anode with a AMEL model 549 potentiostat/galvanostat under constant stirring. The temperature of the mixture and the reaction time were also varied in order to control the synthesis of the nanoparticles. After the desired time, the resulting nanoparticles were obtained by several centrifugation and washing cycles, and finally dried under vacuum for 12 h. Part of the dried sample was heated at 450 °C for 8 h to induce crystallinity .

Measurements

The chronopotentiometry test was conducted with an AUTOLAB PGSTAT 302N system and data were acquired using the NOVA 1.7 software program.

The colloidal properties, in terms the zeta potential, of the synthesized particles before the thermal treatment were studied on a Zetasizer NanoTM, from Malvern Instruments at 25 °C using 10⁻² M KNO₃ as background electrolyte.

The crystalline phase and the size of the crystals analysis of the obtained nanoparticles was performed by X-ray diffraction (XRD) in a D5000 diffractometer equipped with a

secondary monochromator and a SOL-X Bruker detector with Cu-K α radiation. The patterns were collected at room temperature in the range of $10^\circ \leq 2\theta \leq 80^\circ$ with 4° min^{-1} scan rate and the diffractograms were analyzed using the Fullprof suite based on the Rietveld method.

The morphology of the anode after the synthesis was studied by field emission scanning electron microscopy (FE-SEM) on a Philips XL30 S-FEG. The morphologies of the samples were characterized by transmission electron microscopy (TEM), studies were conducted with a JEOL JEM 1010 operating at acceleration voltage of 100 kV.

The thermogravimetric analysis (TGA) of the nanoparticles were conducted with a TA instruments Q500 with $10^\circ \text{C min}^{-1}$ heating rate from room temperature up to 900°C under air flow.

Specific surface area was measured by Brunauer-Emmett-Teller (BET) method using a Micromeritics TriStar II 3020 V1.03 following standard protocols.

The Raman spectra of the anode electrode and of the synthesized nanoparticles were collected using a WITec Confocal Raman microscope System alpha 300R (WITec Inc., Ulm, Germany), equipped with a Nd:YAG laser at a wavelength of 532 nm, with 50 mW laser output power.

For the evaluation of band gap energy of the samples, a UV-VIS spectrophotometer equipped with diffuse reflectance accessory (Perkin-Elmer Lambda 35 spectrophotometer) was employed.

Results and discussions

The synthesis of the titania nanoparticles via electrochemical method (see Figure 1A) was first carried out using a current of 100 mA, at 20 °C and 30 min of reaction time. Sample obtained immediately after the electrochemical reaction, Ti100-30-20, forms transparent colloidal stable solution in water as shown in Figure 1B.

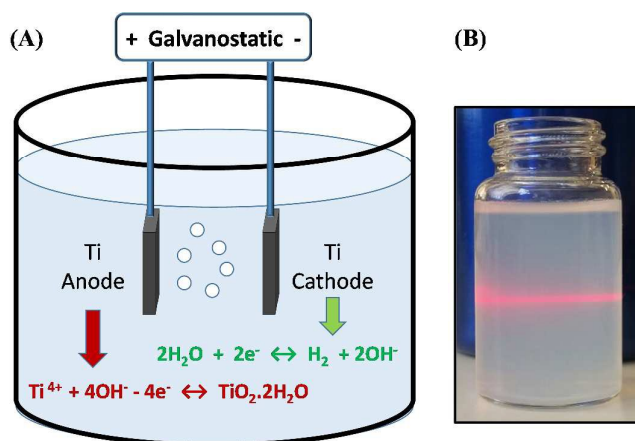


Figure 1. A) Schematic representation of the electrochemical process to synthesize titanium dioxide nanoparticles. B) Photograph shows that the obtained sample exhibits good dispersability in aqueous solution.

The stability of the resulting particles was further studied by zeta potential measurements. It was found that the surface of the particles are both negatively and positively charged depending on the pH, with an isoelectric point around 4.3 (Figure 2). This is in agreement with the values found in literature for TiO_2 nanoparticles (between pH 4 and 6)¹⁵. The change in the surface charge is associated with the proton exchange mechanisms occurring in the hydroxyl groups at the surface of the TiO_2 nanoparticles. Therefore, in principle, the formation of titanium dioxide nanoparticles or a Ti-O material could be expected.

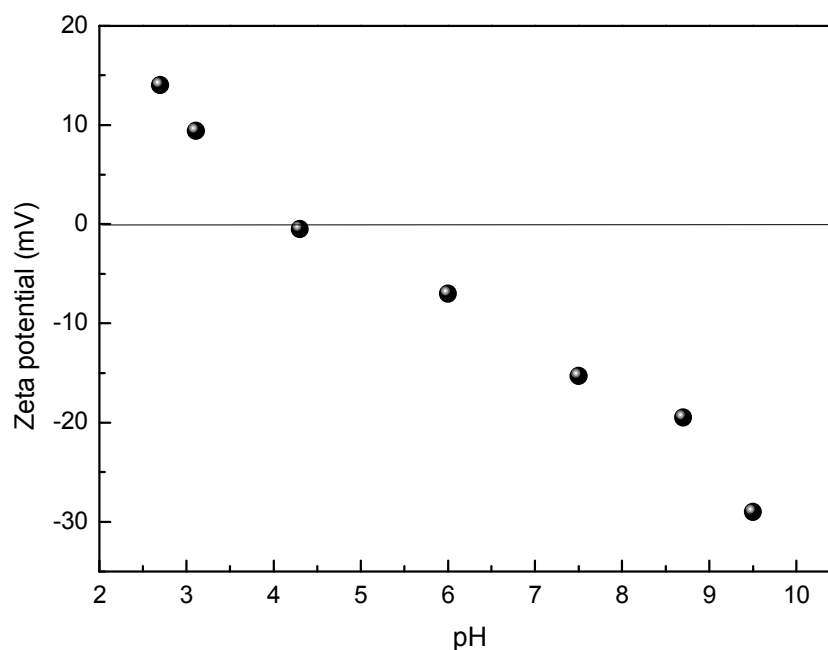


Figure 2. pH dependent zeta potential of colloids titanium dioxide nanoparticles obtained via electrochemical route.

The particles were then washed and dried to be thoroughly characterized. Figure 3A shows the X-ray diffraction pattern of the dried nanoparticles clearly revealing an amorphous phase. Raman spectrum also confirms the amorphous structure of the obtained samples just after the electrochemical synthesis (Figure 3B) with broad bands at frequencies typically detected in amorphous Ti-O materials¹⁶. The bands at 260 and 426 cm^{-1} are ascribed to Ti-O bending, the bands at 600-650 cm^{-1} correspond to the Ti-O stretching while the frequency around 800 cm^{-1} can be ascribed to Ti-O-Ti stretching. Hence, no crystalline structures are directly obtained by this synthetic method. Additionally, it can be observed at higher frequencies several peaks that indicate the presence of organic compounds coming from tetrabutylammonium bromide residues used as electrolyte in the synthesis.

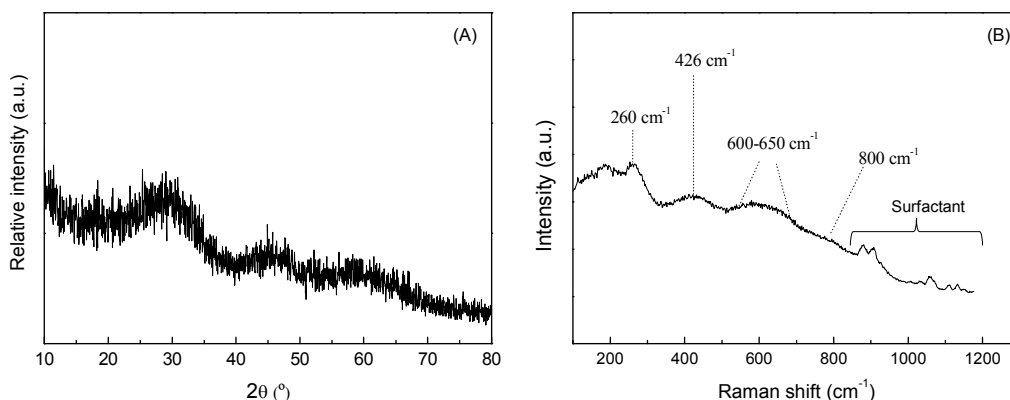


Figure 3. A) XRD pattern and B) Raman spectrum of Ti-O sample synthesized electrochemically.

Besides, TGA analysis of the sample under air atmosphere displayed in Figure 4A exhibits three main weight losses in the temperature range of room temperature to 150 °C and 150-225 °C and 225-480 °C. The first loss of around 15% is presumably due to the removal of water whereas the second weight loss of low percentage could be associated to the densification of the Ti-O amorphous network¹⁷. The third main loss of around 12% can be ascribed to the burning of the organic surfactant present in the sample as previously stated by Raman spectroscopy. Subsequently, TEM images were obtained in a sample prepared by re-dispersion of the Ti-O material in ethanol to study its morphology. As expected from the XRD and Raman measurements, the micrograph reveals the formation of very small particles with size lower than 5 nm, quite aggregated and with irregular shape (Figure 4B).

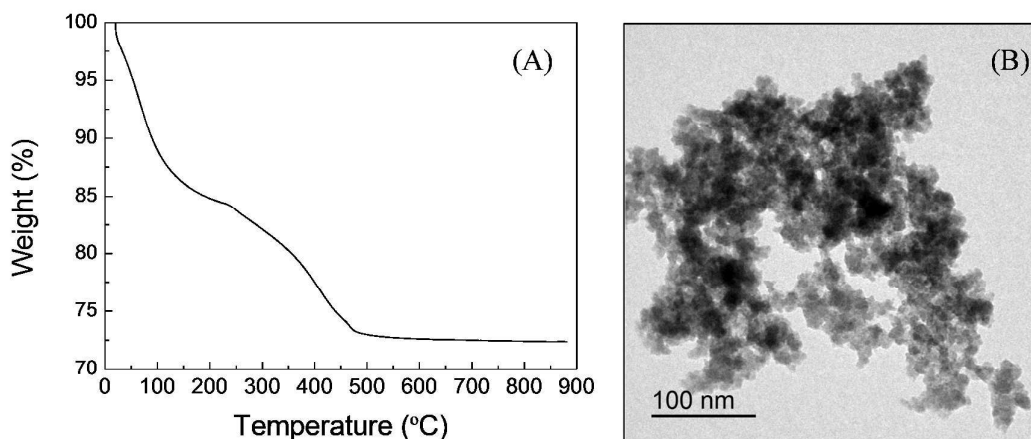


Figure 4. A) TGA analysis in air and B) TEM image of Ti100-30-20 nanoparticles.

The characterization of the powder sample obtained in the electrosynthesis indicates the formation of small and irregular nanoparticles of a Ti-O amorphous material in a very simple and rapid aqueous method. In principle, we could assume that the Ti-O particles are nucleated in the aqueous solution by combination of the Ti cations formed in the anode and the OH^- generated in the cathode as well as the O^{2-} present in the solution. To understand the formation mechanism, the titanium foil surface after the anodization reaction was then analyzed by FE-SEM and Raman spectroscopy. A detailed examination shows that the surface after washing with distilled water becomes rougher with various pores randomly distributed along the surface foil (Figure 5). The inside of the pores appears to be highly broken with numerous cracks.

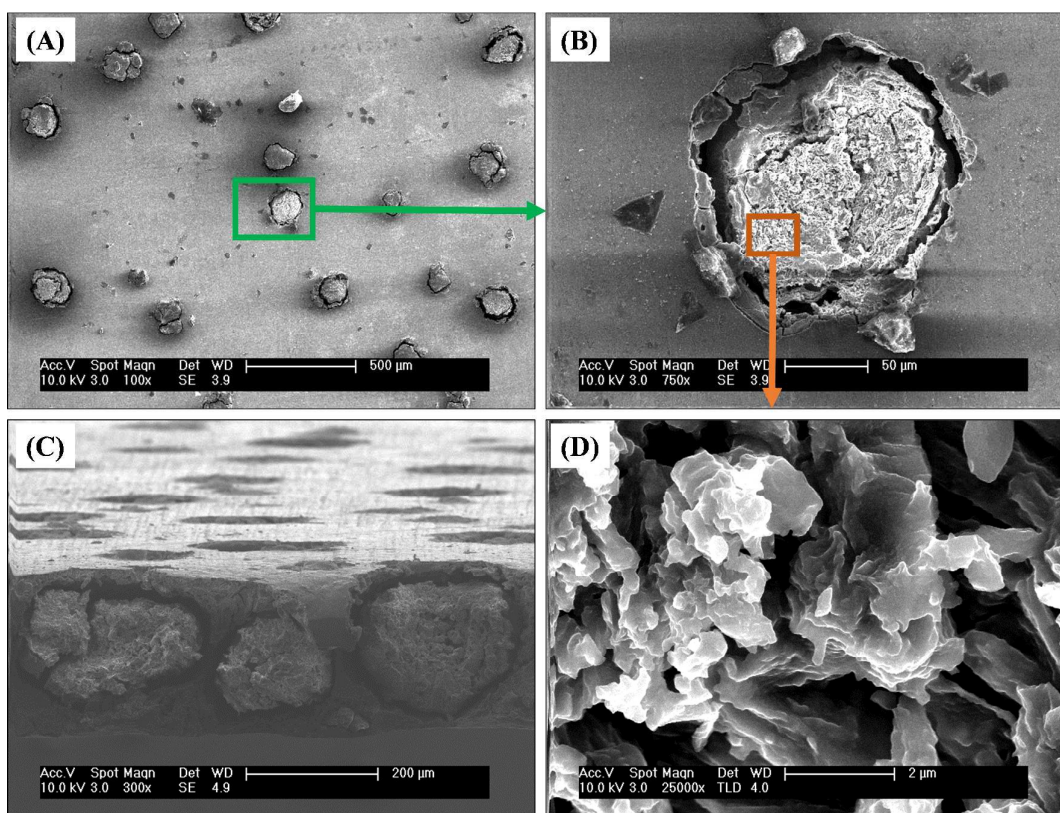


Figure 5. FE-SEM images of titanium foil acting as anode after the electrochemical process at 20 °C, with an applied current of 100 mA during 30 min. Image (B) is the high magnification of the selected region by a rectangle in (A) and image (D) is the high magnification of the selective region in (B). Image (C) is the cross section micrograph of the foil.

The phases developed at the surface as a result of the electrochemical process were evaluated by Raman microscopy, revealing the formation TiO_2 in a mixture of anatase and rutile crystalline phases inside the pores while the rest of the surface remains titanium (Figure 6). However, a small signal corresponding to anatase phase is also observed probably due to the formation of a thin layer of titanium dioxide crystalline phase at the outmost surface.

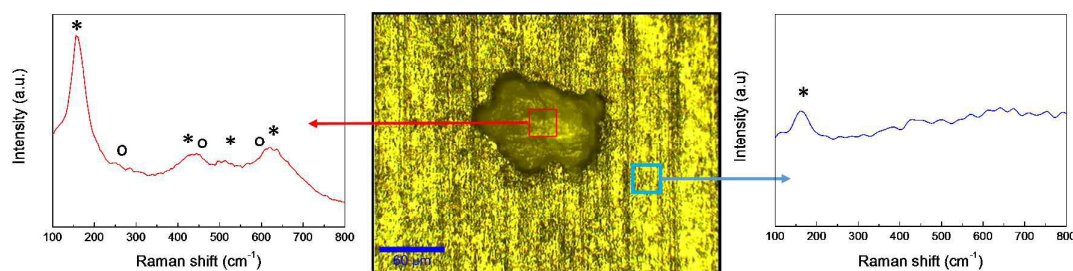
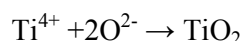
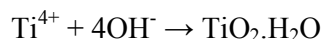
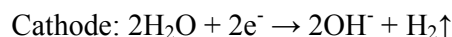
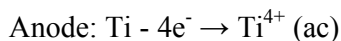


Figure 6. Average Raman spectra of the selected regions of a titanium foil after the electrochemical process at 20 °C with an applied current of 100 mA during 30 min (*-anatase, o-rutile).

Similar surface porous structure has been previously observed and attributed to the formation of TiO_2 at the surface¹⁴. It is well known that a porous TiO_2 layer can be formed on a Ti foil surface by electrochemical anodization, fact that is normally used to fabricate nanotubes¹⁸. The formation of a TiO_2 layer has been also used to create titanium oxide microparticles¹⁹ in solution by electrochemical spark discharge spallation. In this case, the application of a high current provokes a fast anodic reaction on the titanium surface that creates a layer of titanium dioxide, which immediately breaks down to form of anatase titanium oxide microparticles in the aqueous solution. Herein, the current applied density to the electrode is significantly smaller, 50 mA cm^{-2} , and the reaction mechanism is rather different. On one hand, the formation of the crystalline TiO_2 in anatase and rutile structure is probably triggered by the local exothermic heat at the foil caused by of the application of the current at the titanium foil. However in this case, the applied voltage is not high enough to provoke the electrically breakdown of oxide layer, as can be seen in the chronopotentiometry experiment displayed in Figure S1. Thereby the titanium oxide microparticles are not spalled from the surface of the foil, but Ti-O nanoparticles may be formed in the solution. This is supported by the fact that the obtained colloidal nanoparticles are

amorphous Ti-O material as demonstrated by XRD and Raman spectroscopy in contrast with the anatase TiO₂ formed at the surface of the titanium foil. We can propose the formation mechanism of the nanoparticles in the solution as follows:



The pH of the electrolyte solution was measured during the whole electrochemical process corroborating the basic pH as a consequence of the generation of OH⁻ at the cathode electrode.

To further investigate the electrochemical process of generating Ti-O nanoparticles, different parameters of the reaction were varied, i.e. the applied current, the reaction time and the temperature. The experimental conditions of the different reactions are summarized in Table 1.

Table 1. Experimental condition used in the electrochemical synthesis of Ti-O nanoparticles.

Sample	Current (mA)	Reaction Time (min)	Temperature (°C)
Ti50-30-20	50	30	20
Ti100-30-20	100	30	20
Ti150-30-20	150	30	20
Ti200-30-20	200	30	20
Ti100-15-20	100	15	20
Ti100-45-20	100	45	20
Ti100-60-20	100	60	20

Ti100-30-5	100	30	5
Ti100-30-50	100	30	50

Remarkably, the augment of the applied current increases the amount of nanoparticles obtained after the reaction as shown in Figure 7A. Similarly, the quantity of generated material increases with the reaction time and, in a less extends, with the temperature of the solution (Figure 7B and 7C, respectively). In contrast, the shape and the size of the nanoparticles do not vary significantly (data no shown). These features seem to corroborate our previous formation mechanism in which the nanoparticles are formed in the solution caused by the release of the Ti^{4+} from the anode electrode. This release of cation is enhanced by an augment of the current leading to higher amount of Ti-O nanoparticles. In the same way, as the reaction time increases more particle are generated, being this parameter the most determinant. The temperature also favors the process because increases the diffusion of the species.

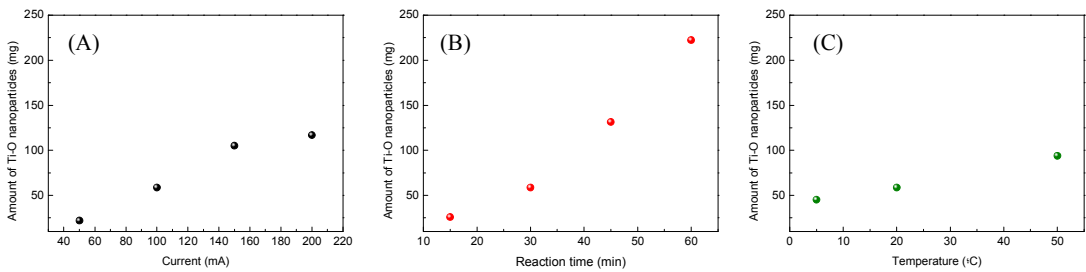


Figure 7. Dependence of the amount of Ti-O nanoparticles with A) current applied (at 20 °C during 30 min), B) reaction time (at 20 °C and a current of 100 mA) and C) temperature (current of 100 mA during 30 min).

The specific energy consumption of the electrochemical synthesis was also analyzed to assess the efficiency of the nanoparticles production, although a scale up of the process should be take into consideration. It was shown that the energy consumption of the

electrosynthesis at room temperature (20°C) varied between 3.0 Kwh/Kg to 12.0 Kwh/Kg depending on the applied current and the reaction time. Figure S2 (see Supplementary Information) shows that the energy consumption per Kg of obtained sample decreases with the current for a fixed reaction time (Figure S3). In contrast, the efficiency of the process increases when the reaction time increases maintaining constant the applied current. Therefore, it seems to be appropriated to perform the synthesis of the nanoparticles with low current and longer reaction time. To further corroborate this aspect a reaction was carried out with an applied current of 25 mA and 2 h of reaction time. Under these conditions, low current and long time, the efficiency of the process is in effect higher than the previous experiments, 1.2 Kwh/Kg. In addition, the electrode consumed was determined by measuring the weight of the electrode before and after the synthesis, with a value of ~0.6 Kg of electrode per Kg of obtained sample.

Once it has been demonstrated the formation of Ti-O nanoparticles via electrochemical route in aqueous solution, the genesis of anatase phase by thermal treatment was next investigated. The amorphous nanoparticles were treated at 450 °C during 8 h under air atmosphere and then were analyzed by XRD and Raman spectroscopy. In effect, after the annealing process the anatase crystallization appears to take place, see Figure 8A. The diffractogram shows the crystal structure of the nanoparticles developed in the sample Ti100-30-20, where all peaks can be indexed to the anatase phase without the appearance other reflections associated to other phases. Rietveld analysis result shows an average crystalline size of c.a. 10 nm. This anatase phase developed after the thermal treatment was also confirmed by Raman spectroscopy. Figure 8B reveals 5 Raman-active mode of tetragonal anatase structure, E_g (146 cm^{-1}), E_g (197 cm^{-1}), B_{1g} (401 cm^{-1}), A_{1g} (518 cm^{-1}) and E_g (635 cm^{-1}).²⁰ Then, it is clearly indicated that the anatase phase is well developed after calcination, which is consisted with the XRD measurement.

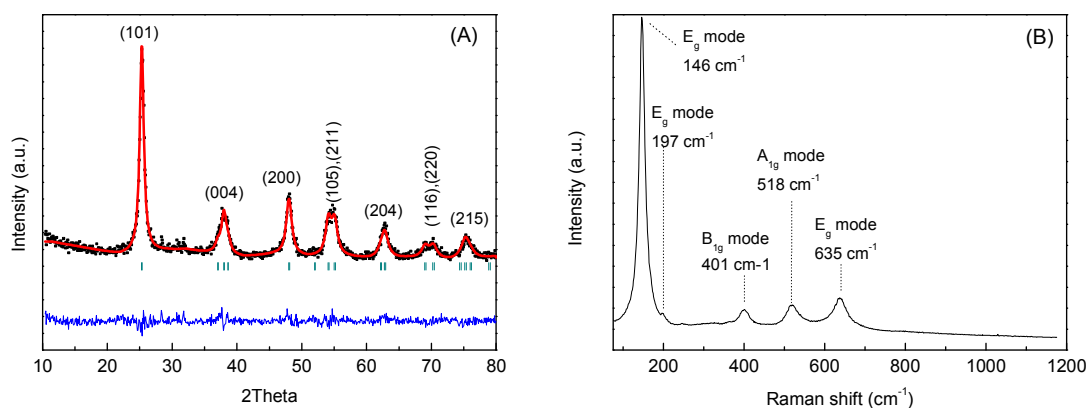


Figure 8. (A) X-ray diffractogram of the sample Ti100-30-20 after the thermal treatment. The black dots show the observed data and the red line shows the calculated pattern obtained using the Rietveld analysis. The trace under the diffractogram shows the difference between the observed and calculated patterns. Bragg positions are marked (|). (B) Raman spectrum of the Ti100-30-20 after the thermal treatment.

The increase in the particle size with respect to the as-prepared Ti-O particles as a consequence of the crystallization induced by the thermal treatment was also observed by TEM. Figure 9 shows the TEM images of Ti100-30-20 and Ti200-30-20 samples after calcination, with particle size of around 12 ± 2 nm. It has to be mentioned that the particle size determined by both DRX and TEM does not varied significantly with the experimental conditions used for the as-prepared samples. This was expected because the Ti-O amorphous nanoparticles showed similar structures independently of the parameters used in the synthesis. Besides, the specific surface area of the TiO₂ nanoparticles after the thermal treatment was measured by BET analysis, which was estimate to be 90 m²/g, a relative large value.

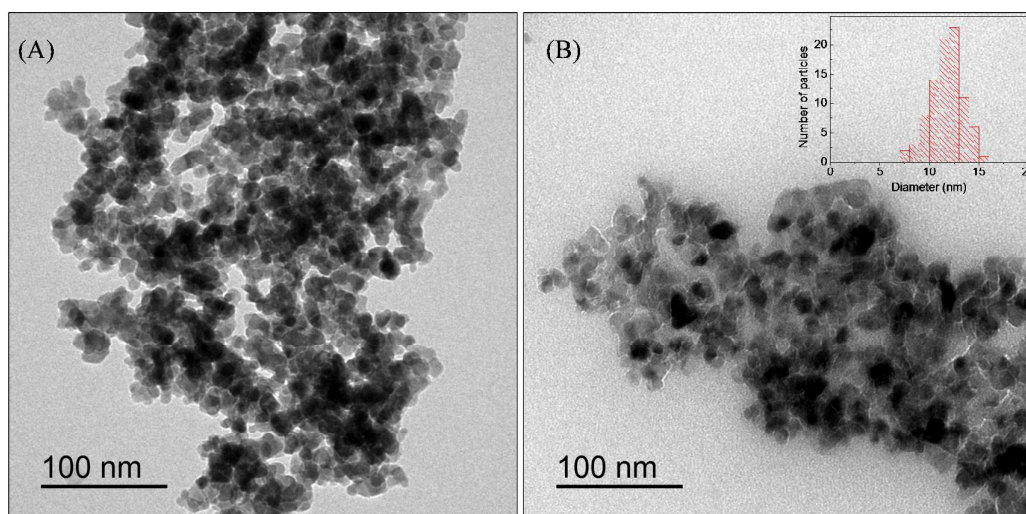


Figure 9. TEM images of (A) Ti100-30-20 and (B) Ti200-30-20 after calcination. The inset shows the corresponding particle size distribution.

Subsequently, diffuse reflectance UV-Vis spectroscopy was employed to study the optical properties of the anatase TiO_2 nanoparticles synthesized by electrochemical route followed by thermal treatment in comparison with the as prepared samples. The reflectance spectra were analyzed using the Kubelka-Munk relation that transform the measured reflectance into a Kubelka-Munk function, K , which can be associated to an absorption coefficient:

$$K = \frac{(1 - R)^2}{2R}$$

where R is the reflectance. As an example, Figure 10A shows the measurements for the sample Ti100-30-20 before and after calcination. In both cases, it is clearly appreciated a sharp decrease in the K in the ultraviolet region attributed to the band gap transition. Interestingly, a red shift in the absorption edge is observed after calcination and development of the anatase phase. Then, the bandgap energies of the samples were estimated from the variation of the Kubelka-Munk function with photon energy, $(K \cdot hv)^{0.5}$ versus $hv^{21,22}$, (see Figure 10B). The calculated band gaps of Ti-O amorphous

and TiO₂ anatase NPs are 3.27 and 3.05, respectively, which are consistent with values found in literature^{23,24,25,26}.

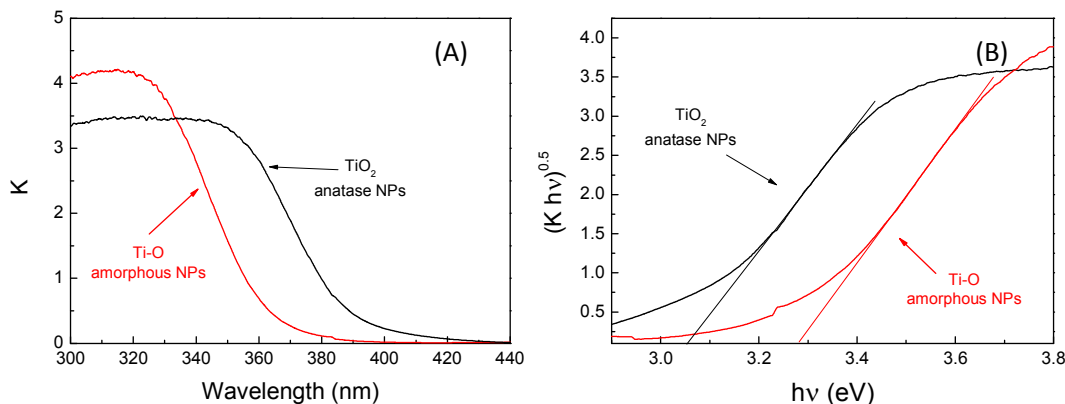


Figure 10. A) Diffuse reflectance spectra and B) transformed Kubelka–Munk function versus the photon energy of TiO₂ anatase (Ti100-30-20) and Ti-O amorphous nanoparticles.

The optical properties of the rest of the synthesized nanoparticles were also analyzed showing similar band gap values, 2.95-3.10 for the TiO₂ anatase sample and 3.23-3.30 for the amorphous samples. The band gap energies of the as prepared NPs do not follow any trend as function of the synthesized parameters, temperature, reaction time and applied current; thus, it is suggested that the experimental parameters investigated only have an influence on the reaction yield, as demonstrated above. Likewise and as expected, the anatase NPs obtained after calcination present very similar values independently of what experimental conditions were employed for the electrochemical synthesis.

Conclusions

In summary, we have developed a fast and facile method to synthesize titanium dioxide nanoparticles in aqueous medium. Briefly, this approach consists in the galvanostatic

electro-oxidation of titanium foil in an electrolyte aqueous, which provides a colloidal stable solution of amorphous Ti-O nanoparticles. As an advantage over other methods, low current, very mild experimental conditions and short reaction times are required. It is also demonstrated that the reaction yield of the method can be augmented by increasing the synthesis time, temperature or current applied to the electrode. Besides, TiO₂ nanoparticles of around 10-15 nm and pure anatase crystalline phase can be easily obtained by thermal treatment of the as prepared samples. This calcination of the nanoparticles induces the crystallization process, increases the particle size and also decreases the band gap energy with values between 2.95 and 3.10 eV. Therefore, this current method creates a new route to prepare titanium dioxide nanoparticles with good photocatalyst properties.

Acknowledgments

The authors gratefully acknowledge the MINECO (Projects MAT2012-37109-C02-02 and MAT2013-48009-C4-1-P) for financial support. A. Muñoz-Bonilla also thanks the MINECO for her Ramon y Cajal contract.

References

1. A. Fujishima, T. N. Rao, and D. a. Tryk, *J. Photochem. Photobiol. C Photochem. Rev.*, 2000, **1**, 1–21.
2. X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959.
3. X. Chen, L. Liu, and F. Huang, *Chem. Soc. Rev.*, 2015.
4. M. Cargnello, T. R. Gordon, and C. B. Murray, *Chem. Rev.*, 2014, **114**, 9319–9345.
5. K. Madhusudan Reddy, C. V. Gopal Reddy, and S. V. Manorama, *J. Solid State Chem.*, 2001, **158**, 180–186.
6. A. Pottier, S. Cassaignon, C. Chanéac, F. Villain, E. Tronc, and J.-P. Jolivet, *J. Mater. Chem.*, 2003, **13**, 877–882.

7. S. Lee, I. S. Cho, J. H. Lee, D. H. Kim, D. W. Kim, J. Y. Kim, H. Shin, J. K. Lee, H. S. Jung, N. G. Park, K. Kim, M. J. Ko, and K. S. Hong, *Chem. Mater.*, 2010, **22**, 1958–1965.
8. H. Cheng, J. Ma, Z. Zhao, and L. Qi, *Chem. Mater.*, 1995, **7**, 663–671.
9. K. Yanagisawa and J. Ovenstone, *J. Phys. Chem. B*, 1999, **103**, 7781–7787.
10. C. L. Chen, C. Dong, C.-H. Chen, J.-W. Wu, Y.-R. Lu, C.-J. Lin, Y. H. S. Liou, C.-M. Tseng, K. Kumar, D.-H. Wei, J. Guo, W.-C. Chou, and M.-K. Wu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22064–22071.
11. V. Zwillling, E. Darque-Ceretti, a. Boutry-Forveille, D. David, and M. Y. Perrin, *Surface Interface Anal.*, 1999, **27**, 629–37.
12. S. Karuppuachamy, *Solid State Ionics*, 2002, **151**, 19–27.
13. S. Ashok Kumar, P.-H. Lo, and S.-M. Chen, *Nanotechnology*, 2008, **19**, 255501.
14. Y. Tang, D. Gong, Y. Lai, Y. Shen, Y. Zhang, Y. Huang, J. Tao, C. Lin, Z. Dong, and Z. Chen, *J. Mater. Chem.*, 2010, **20**, 10169.
15. M. D. Chadwick, J. W. Goodwin, E. J. Lawson, and P. D. A. Mills, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2002, **203**, 229–236.
16. M. Fernandez, X. Wang, C. Belver, and J. C. Hanson, *J. Phys. Chem. C*, 2007, **111**, 674–682.
17. D. Eder and A. H. Windle, *J. Mater. Chem.*, 2008, **18**, 2036.
18. A. Ghicov and P. Schmuki, *Chem. Commun. (Camb.)*, 2009, 2791–808.
19. B. Zhao, F. Chen, Y. Jiao, and J. Zhang, *J. Mater. Chem.*, 2010, **20**, 7990.
20. J. Yan, G. Wu, N. Guan, L. Li, Z. Li, and X. Cao, *Phys. Chem. Chem. Phys.*, 2013, **15**, 10978–88.
21. H. Lin, C. Huang, W. Li, C. Ni, S. Shah, and Y. Tseng, *Appl. Catal. B Environ.*, 2006, **68**, 1–11.
22. S. Sakthivel and H. Kisch, *Angew. Chemie - Int. Ed.*, 2003, **42**, 4908–4911.
23. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253–278.
24. K. Kaur and C. V. Singh, *Energy Procedia*, 2012, **29**, 291–299.
25. S. Pan, X. Liu, M. Guo, S. F. Yu, H. Huang, H. Fan, and G. Li, *J. Mater. Chem. A*, 2015, **3**, 11437–11443.
26. H. H. Pham and L.-W. Wang, *Phys. Chem. Chem. Phys.*, 2015, **17**, 541–550.

Graphical Abstract

