

Chemical Structure of TiO Organometallic Particles Obtained by Plasma

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ABSTRACT

This work presents a study about the chemical structure of titanium oxide (TiO) particles synthesized by plasmas using titanium tetrapropoxide, $\text{Ti}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3)_4$. In plasmas, practically all chemical bonds are susceptible to participate in the reactions producing different results than those obtained by the traditional chemical routes. The particles obtained this way are semispheres and fibers grouped in random and layered structures in the 120 - 500 nm interval and mean diameter of 86.4 nm (fibers) and 308.6 nm (semispheres). The analysis of the resulting TiO structure was performed by IR and XPS finding that the main chemical state of Ti in these conditions was $\text{O}_2\text{-Ti-O}_2$ (Ti surrounded by O) which is part of the precursor structure, however, in O, the main chemical state was Ti-O-Ti formed with the rupture of the precursor Ti-O-C bonds. These last bonds reduce the conjugation between the structure of both elements, $\text{O}_2\text{-Ti-O}_2$ and Ti-O-Ti , to produce organometallic compounds. Other chemical states appeared showing consecutive dehydrogenation steps during the synthesis with the formation of multiple bonds as a consequence of the continuous collisions in the plasma. These results allow us to follow the chemical reactions promoted by this kind of plasmas to produce TiO nanoparticles which are essentially conformed of intensive dehydrogenation.

Keywords: TiO; Particles; Plasma; Degradation; XPS; TTP

1. Introduction

Under plasma conditions, degradation and/or synthesis of materials can be carried out with different results than those obtained by the traditional chemical routes. This is because in plasmas the accelerated electrons can reach kinetic energies beyond the bonding energy of the atoms promoting, by collisions, chemical reactions among radicals and/or ions without involving other reagents or substantially increasing the temperature of the synthesis which could damage the reagents [1]. Plasma techniques have already been used to prepare amorphous and/or crystalline phases of titanium oxides [2]. In these conditions, the TiO_x configuration of crystalline phases in which $x = 2$ can be displaced from 2 to other ratios, obtaining materials generically known as TiO.

Some photochemical applications of TiO are based on its capacity to absorb an incident light transferring part of

this energy to other materials through its surface. This energy can be applied to oxidize molecules or to create free radicals in other substances to be used in the oxidation or in degradation of contaminants [3,4]. In this superficial activity, materials with TiO need to have a large superficial area, as in nanoparticles.

Spherical TiO nanoparticles produced by chemical techniques with titanium tetraisopropoxide (TTIP) have been obtained with diameters below 100 nm with characteristics depending on the precursor and on the type of synthesis [5-9]. The main precursors of TiO nanoparticles in chemical syntheses up to now have been TTIP [10,11] and TiCl_4 [12,13]. In plasma syntheses, commercially pure titanium oxidized in Ar/O mixtures [14] and TTIP degraded in resistive coupling discharges [15] have been used. Plasma degradation of titanium tetrapropoxide (TTP), $\text{Ti}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3)_4$, to produce organometallic particles has also been focused on the electric properties and on the amorphous structure of the particles [16,17]. Now,

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in this work, the chemical structure of TiO particles synthesized by plasma glow discharges of TTP and water in gas-phase is studied with IR and XPS spectroscopies with the objective of exploring the different steps of TTP degradation under the plasma collisions which promote the formation of TiO organometallic nanoparticles.

2. Material and Methods

The degradation of TTP to produce TiO was obtained with water vapor plasmas through the constant collisions of accelerated ions and electrons in the plasma to reduce the organic part of TTP molecules and to increase the metal oxide fraction. Due to the polarity, the electrons tend to collide with the most electropositive segments in TTP, and depending on the energy applied; this effect may produce the breaking and formation of new chemical bonds promoting the formation of TiO compounds.

This process was made in a vacuum tubular glass reactor, 9 cm diameter and 20 cm length, with stainless steel flanges and electrodes, which are plates of 6.5 cm in diameter separated by 8 cm. The electric discharges were produced with resistive coupling in the 0.3 - 0.9 mbar interval at 13.56 MHz, 240 min and 100 W. As TTP (Aldrich, 98%) is a volatile and reactive liquid at room conditions, it was spread over a sample holder, frozen with liquid nitrogen at approximately -180°C and placed inside the reactor between the electrodes. This procedure was intended to reduce the reactivity and evaporation of TTP to prepare the electric discharges with water, which was introduced into the reactor from another recipient and vaporized due to the difference of pressure between the recipient and the reactor. The heat produced by the discharges slowly increased the temperature in the reactor and vaporized the frozen TTP, which reacted with the particles in the gas-phase. The synthesis process of TiO is described in the flow chart of **Figure 1**.

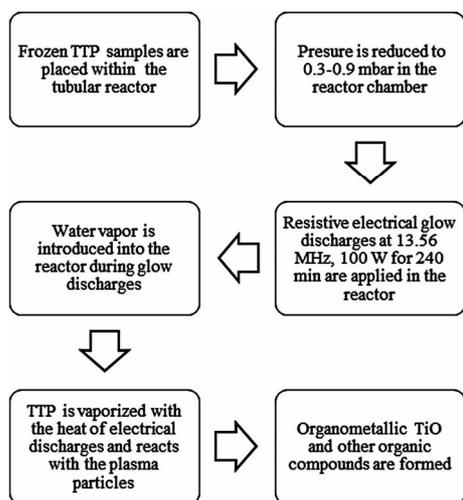


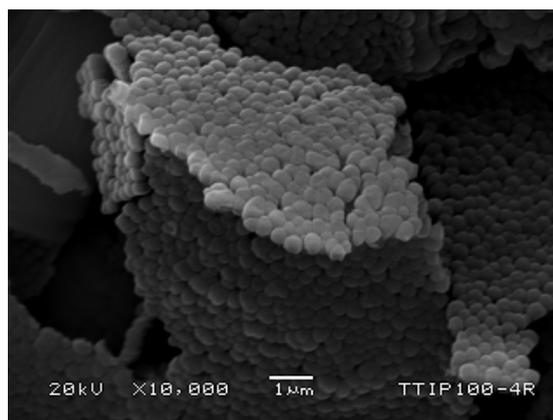
Figure 1. Flow chart that describes the synthesis of TiO.

During the synthesis, the inorganic fraction remained on the sample holder, but the smallest organic molecules evaporated from the holders. However, some organic fragments reacted among them to form large molecules which are difficult to evaporate. These fragments formed complex organometallic compounds in the final TiO powder. No further treatment was done to the titanium oxide obtained after the syntheses. The characterization of the TiO particles was focused on the chemical structure and morphology.

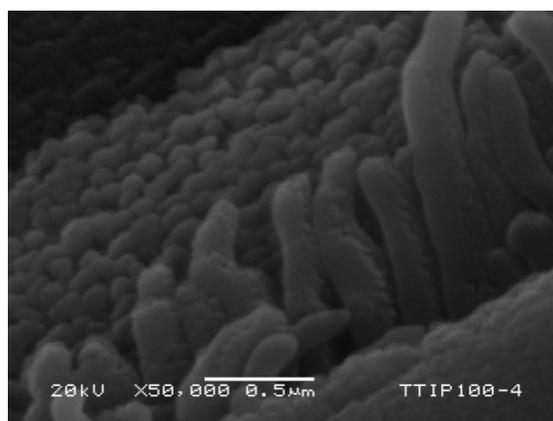
3. Results and Discussion

3.1. Micro Morphology

Figure 2 is composed of 2 images of scanning electron microscopy (Jeol 5900 LV) of TiO particles taken at $10,000\times$ and $50,000\times$. The images show semispherical, **Figure 2(a)**, and fibered particles, **Figure 2(b)**, arranged in layers or in agglomerates of fibers with diameters from 25 to 500 nm.



(a)



(b)

Figure 2. Different morphology in TiO particles. (a) Monolayers of semispherical particles with an average diameter of 308.6 nm grown with different orientation; (b) Agglomerates of fibers aligned in approximately the same direction with an average diameter of 86.4 nm.

Both morphologies were obtained in the same experimental conditions. The spherical particles form surfaces of layered structures with different orientation. The diameter distribution is between 120 and 500 nm [15] with a center at 308.6 nm, see **Figure 2**. These particles have the largest average. The fibered structures were formed as groups of consecutive particles stacked in one direction. The alignment may be promoted by the electric field applied to the reactor. The diameter of fibers slightly decreases on top, which is in the 25 - 230 nm interval with center at 86.4 nm, see **Figure 2(b)**. Fibers with length up to 1 μm were observed in the micrographs.

Figure 3 shows the histogram of frequencies of each group with the arithmetic mean of diameters (ϕ). The histogram shows that the greater diameter and wider distribution belong to the particles, however, in the 150 - 200 nm diameter interval, both structures can be found.

3.2. Chemical Structure of Titanium Oxides

The TTP molecule has a central atom of Ti surrounded by four oxygen atoms, this structure is related to the inorganic part, each oxygen atom has a chain of three carbons that corresponds to the organic fraction, the molecule of TTP can be written as $\text{Ti}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3)_4$. The chemical structure of TiO particles obtained in the synthesis was analyzed with a Thermo Scientific Nicolet iS5 FTIR spectrophotometer in ATR mode with a diamond cell in the 550 - 4000 cm^{-1} interval using 150 scans, see **Figure 4** where TTP is in black and TiO in blue.

The absorption of C-H groups in TTP can be seen in the following wavenumbers, 2956, 2870, 988, 887 and 783 cm^{-1} . The other absorptions belong to C-O in 1377 and 1071 cm^{-1} , and to the C-C structure, 1472 cm^{-1} . The most important group for this work is located in the wide

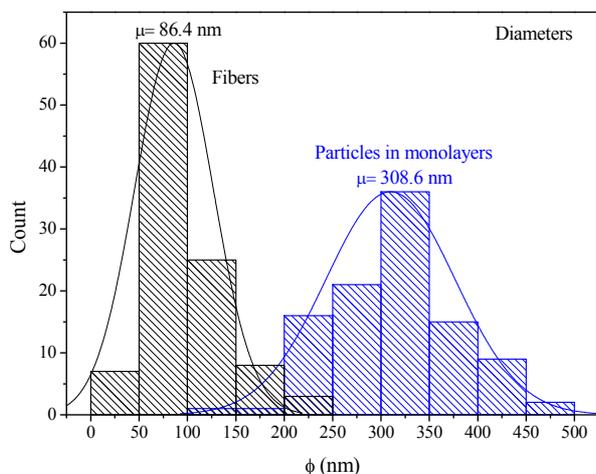


Figure 3. Diameter distribution frequency histogram of semispheres and fibers. The fiber diameter is centered in 86.4 nm and in particles is centered in 308.6 nm.

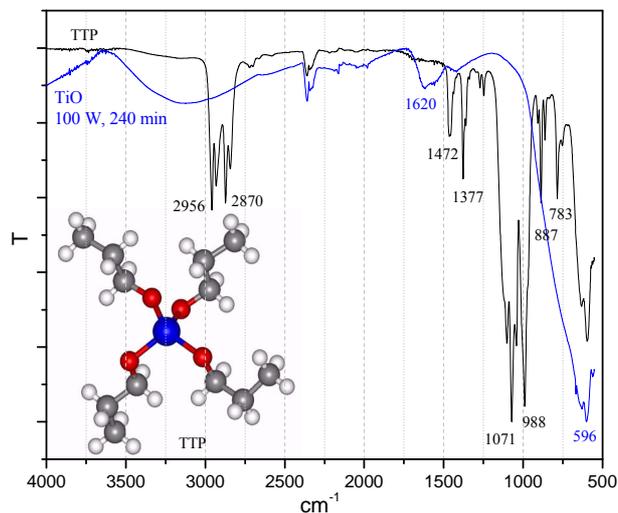


Figure 4. IR spectra of TTP (in black) and TiO (in blue) synthesized by plasma. Note that the organic phase in TiO was greatly reduced leaving the most intense absorption to Ti-O bonds. In the TTP molecule, Ti is in blue, O in red, C in grey and H in white.

signal centered at 596 cm^{-1} , which is part of the Ti-O absorption in TTP and TiO. This wide signal has been reported before centered around 550 cm^{-1} for TiO_2 obtained from TiCl_4 [18].

In TiO, many C-H groups of TTP disappeared or reduced to very low expressions, leaving the Ti-O absorption as the most important. Other groups not present in TTP appeared in TiO as a consequence of the plasma reactions. The wide absorption centered in 3135 cm^{-1} includes three groups, O-H, =C-H and -C-H.

The first one belongs to the interaction with water in the plasma, =C-H groups appear as a consequence of dehydrogenation reactions due to the collisions of the particles in the plasma, and -C-H groups are remnants of TTP in TiO. Other groups in TiO that can be seen in the absorption centered in 1620 cm^{-1} are -C=C and -C=O, which are also a consequence of the dehydrogenation reactions. The release of H atoms produces free radicals, and if two of them are sufficiently near, both neutralize forming multiple bonds.

3.3. Superficial Elemental Analysis

The superficial elemental analysis and the energetic distribution of Ti2p, O1s and C1s orbitals in TiO was obtained with a monochromatic Al X-ray (1486.6 eV) Thermo K-Alpha photoelectron spectroscope. The samples remained in a pre-analysis chamber for approximately 1 hr at 10^{-3} mbar before entering the analysis chamber. The diameter of the analysis area was 400 μm .

The electrostatic charges in the samples were reduced with a beam of Ar ions which increased the base pressure from 10^{-9} to 10^{-7} mbar in which the XPS analyses were

performed. The elements involved in the analyses were Ti, O, C and N and are presented in **Figure 5** in survey mode. This last element has a small participation (0.46%) and can be due to the atmospheric interaction. The elemental content of Ti is 16.91% and O is 46.34% with an $x = 2.74$ (O/Ti atomic ratio). This means that there are less oxygen atoms than in TTP molecules ($x = 4$), but more than in TiO_2 compounds with crystalline phases ($x = 2$). However, O atoms can bond to C and Ti, which displace the O/Ti ratio from 2. The content of C atoms was reduced from 70.58% in TTP to 36.29% in TiO indicating that the degradation of TTP molecules worked in at least 50%.

3.4. Chemical States in TiO

The analysis of the chemical states in TiO particles was based on the electronic energetic distribution of Ti2p, O1s and C1s orbitals and on different chemical states that may appear with the degradation of TTP molecules in plasmas. The specific energetic atomic states were studied adjusting the distribution of the orbitals with internal Gaussian curves considering the full width at half maximum (FWHM) parameters based on the Crist work for advanced fitting of monochromatic XPS spectra [19]. As the internal curves become wider, more chemical states can be included in them.

Each energetic state can be associated with atomic chemical states involving all bonding orbitals shared in the atoms, and although the bonding orbitals are in the exterior electronic shell and the orbitals analyzed in XPS are further inside the atomic structure, any modification in the valence orbitals adjust the energetic equilibrium of the entire atom, modifying the orbitals studied in the XPS analysis. Neighboring atoms also exert influence in the energetic distribution of the atoms, although they are

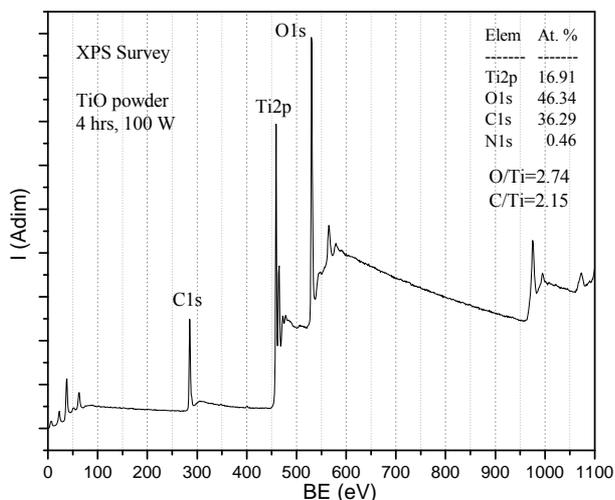


Figure 5. XPS survey of TiO powder. The elemental content and atomic ratios are included.

not directly bonded. Thus, in analyzing the energy distribution of orbitals, the whole chemical environment has to be considered.

The scattered points in the following graphs represent the electronic binding energy (BE) of orbitals obtained with the spectroscope, the blue internal curves represent the deconvoluted distribution of the orbital and the red line represents the sum of all adjusted curves along BE. The representation of the atomic chemical states in this work was done including all the possible bonding combinations. The notation used in this work indicates that the atom in bold face is bonded with all atoms in the formula. For example, the most common chemical state of Ti in TiO is $\text{O}_2\text{-Ti-O}_2$, in which the central Ti atom is bonded in its own spatial configuration with 4 O atoms. In the same trend, $\text{C-CH}_2\text{-C}$ represents a C atom surrounded by 2 C and 2 H atoms, and $\text{C}_3\text{-C-H}$ indicates a C atom surrounded by 3 C and 1 H atom. If it is possible, both sides of the central atom are used to clarify the structure.

3.5. Ti Chemical States

Ti chemical states were studied with the energetic distribution of Ti2p 3/2 orbitals, see **Figure 6**. Ti2p has a bimodal electronic distribution belonging to the 1/2 and 3/2 orbitals [20], in which the most intense signal belongs to the 2p 3/2 orbital, which is studied in this work. The 3/2 orbital was observed from 456.5 to 460.6 eV and was adjusted with 3 internal gaussian curves, $\text{FWHM} \leq 1.05$ eV, which represent 3 Ti energetic states.

The greatest participation, 84.31%, was obtained with Curve 2 centered at 458.74 eV, which can be assigned to Ti surrounded by oxygen atoms, $\text{O}_2\text{-Ti-O}_2$. This state is also the core of TTP molecules and it is found in the ma-

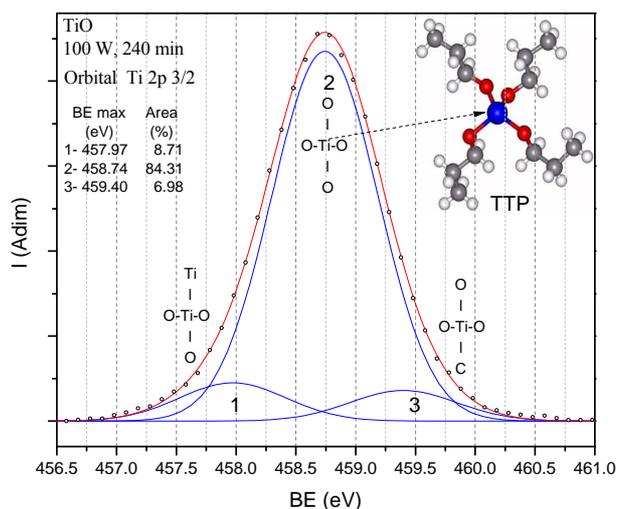


Figure 6. Energetic distribution of Ti2p 3/2 orbital in TiO particles. Note that the main Ti chemical state in TTP, $\text{O}_2\text{-Ti-O}_2$, was preserved in 84.31% in the final compounds.

jority of titanium oxides as well. The percentage suggests that the main structure of Ti in TTP prevailed after the synthesis. However, the experimental curve indicates that at least 2 more energetic states participate in the particles, which can be identified as the superposition of $O_3\text{-Ti-Ti}$ and $O_3\text{-Ti-H}$ states centered at 457.97 eV with 8.71%, see Curve 1. The other chemical configuration is $O_3\text{-Ti-C}$ centered at 459.40 eV with 6.98%, see Curve 3.

All states indicate that there are ruptures of some Ti-O bonds of the TTP structure to form Ti-Ti, Ti-H and Ti-C new bonds in small percentages during the synthesis of TiO particles by plasma.

3.6. O Chemical States

The analysis of O chemical states was supported in the unimodal energetic distribution of O1s orbitals shown in **Figure 7**. The O1s energetic distribution consists of the 528.5 - 534.3 eV interval and was adjusted with 4 curves considering $\text{FWHM} \leq 1.2$ eV. The greatest area belongs to curve 1 centered at 530.19 eV, which can be assigned to Ti-O-Ti and C-O-Ti chemical states with 71.71% area. Curve 2 can be related to C-O-Ti and C-O-H centered at 531.32 eV, 13.83%. The energy required in the formation of C-O-Ti chemical states derived from the degradation of TTP is located between the formation energy of Ti-O-Ti and C-O-H states. This is the reason why C-O-Ti is related with both, Curves 1 and 2.

C-O-C can be identified in Curve 3, centered at 532 eV, with 9.89%, and finally C=O can be associated with Curve 4 centered in 533 eV with 4.57% area. Ti-O-Ti states are not part of the TTP structure and were formed during the synthesis of TiO particles with the constant breaking and formation of chemical bonds due to the collisions among particles in the plasma, especially, the

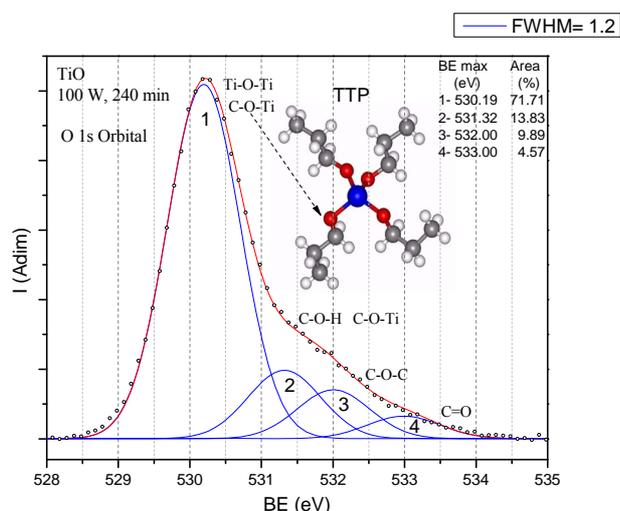


Figure 7. Energetic distribution of O1s orbitals in TiO particles. The Ti-O-Ti chemical state was not part of the original precursor and appeared after the plasma treatment.

breaking and rearrangement of some Ti-O bonds, which occurs as the main transformation of the initial C-O-Ti arrangement in TTP.

Ti-O-Ti and $\text{O}_2\text{-Ti-O}_2$ states in different conjugated arrangements can be found in crystalline TiO oxides. The percentage of Ti-O-Ti , 71.71%, can be related with the efficiency of the synthesis. On its part, C-O-Ti is part of the TTP structure that survived the energy of the discharge. This is an indicative of the organometallic character of particles. The other chemical states, C-O-H and C=O , were formed during the synthesis and are part of the organic fraction in the final compounds.

3.7. C Chemical States

The C chemical states resulted after the TiO synthesis were studied with the C1s unimodal energy distribution from 283 to 290.2 eV adjusted with 5 gaussian curves using the restriction of $\text{FWHM} \leq 1.1$ eV, see **Figure 8**.

The curve with the lowest energy is centered at 284.06 eV, 8.01% area, which represents the chemical arrangements: H-C-C_3 , Ti-C-C_3 , and if there are some remnants of the precursor, such as $\text{C-CH}_2\text{-O}$ and $\text{C-CH}_2\text{-C}$ [21], they will be in this curve in small proportion, which has the most hydrogenated configurations of C.

The presence of Ti-C bonds suggests that most chemical bonds in TTP can be broken by the plasma to form new structures, because it needs the rupture of Ti-O bonds, which have the highest bonding energy in TTP, 6.86 eV. The greatest participation belongs to Curve 2 centered in 284.85 eV, 54.96%, which can be assigned to $\text{C}_2\text{-C-C}_2$ and $\text{C}_3\text{-C-O}$, both with formation energy between 14.4 and 14.3 eV. The difference with the states of the first curve is the replacement of one H for one C atom as a consequence of the dehydrogenation promoted

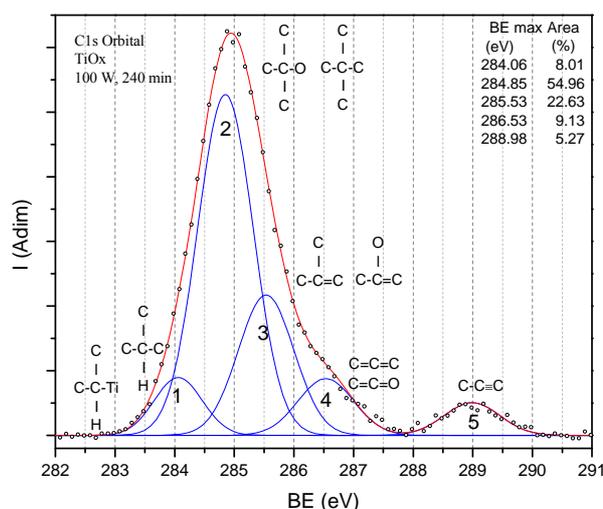


Figure 8. Energetic distribution of C1s orbitals in TiO particles. Most of C chemical states were formed during the synthesis of TiO.

in the plasma. Note that these states do not have hydrogen atoms and have a great participation in the final compounds.

The next Curve 3 at higher BE is centered at 285.53 eV, 22.63%, and can be associated with double bonds involving C=CO-C and C=C-C₂ structures. The formation of multiple bonds can also be due to dehydrogenation in consecutive C atoms in the TTP organic arms as a consequence of the collisions in the plasma, and to the neutralizations of the radicals left behind. More combinations of double bonds appear in Curve 4 which is centered at 286.53 eV, C=C=C and O=C=C, due to other steps in the dehydrogenation process. These bonds are signals of complex structures, in which the final states can be related with triple bonds as C-C≡C which can be found in Curve 5 centered at 288.98 eV. These chemical states represent the final oxidation stage of the organic segment in the plasma conditions applied to the synthesis.

In general terms, the energetic distribution of C1s orbitals suggests that many carbon chemical states may appear in the particles product of the plasma reactions. These states show a gradual oxidation of the TTP organic arms in consecutive dehydrogenation steps with the formation of multiple bonds and complex structures as a consequence of the continuous collisions in the plasma.

4. Conclusions

Usually, the synthesis of TiO by plasmas is done by oxidizing Ti with oxygenated combinations of gases to produce thin films of TiO on the surface. However, in this work, TiO particles were synthesized modifying the structure of titanium tetrapropoxide by plasma to separate its organic and inorganic components. In these conditions, spherical and fibered organometallic particles were obtained with diameters between 120 and 500 nm grouped in random and layered arrangements. The arithmetic mean diameter of fibers and spheres was 86.4 and 308.6 nm, respectively, and the maximum length of fibers was approximately 1 μm.

The chemical structure of the particles and the mechanism of formation were studied through the distribution energy of Ti2p, O1s and C1s orbitals. The main chemical states found in these conditions were O₂-Ti-O₂, in which Ti is surrounded by O, and Ti-O-Ti, which is O surrounded by Ti. This state was not part of the original TTP precursor and is the main modification of the plasma reactions to produce TiO particles. Both states usually produce conjugated structures of titanium oxides. However, other chemical states appeared with combinations of C, O and H, as O₃-Ti-C and C-O-Ti, which are remnants of the TTP precursor, that randomly inserted in the structure reduce the conjugation between O₂-Ti-O₂ and Ti-O-Ti producing organometallic compounds.

Chemical states in C with multiple bonds in different combinations were formed, which are signals of consecutive dehydrogenation steps in the molecules with the accelerated particles in the plasma. These carbon chemical states allow us to follow the mechanisms of reaction in plasma conditions, which are essentially conformed of intensive dehydrogenation.

5. Acknowledgements

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