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Synthesis of titanium oxide nanoparticles by plasma

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This work presents a study about the evolution of titanium oxide particles synthesized with glow discharges of water and Tetra Titanium Propoxide (TTP). The syntheses involved sequential changes of TTP from solid, liquid and vapor phases under resistive glow discharges at 13.56 MHz, 0.5-0.8 mbar and 100 W with reaction times between 60 and 240 min. The reaction of TTP and water between the electrodes originated titanium oxide powder composed of white particles with diameter between 106 and 695 nm and different geometries depending on the time of synthesis. These materials may have environmental applications in the sorption of toxic contaminants.

Keywords: Titanium oxide; Nanoparticles; Plasma

1. Introduction

Titanium oxide compounds have applications in superficial photo-catalysis [1-3] because depending on the incident wavelength they form reactive $(OH)^-$ groups useful in the conversion of complex to simpler organic compounds [4-7]. This process can be applied in the degradation of toxic pollutants [8] using large active surfaces that can be obtained synthesizing titanium oxides in nanoparticles. TiO_2 compounds with morphologies at nanometric scale have been obtained by different chemical methods, nanotubes with 10-20 nm diameter and 50-80 nm length [9], nanofibers of 20-100 nm in diameter and up to 10 μm in length [10] and nanoparticles of 30-50 nm in diameter [11]. TiO_2 amorphous compounds have also been obtained with surface in the 79-385 m^2g^{-1} interval [12].In the area of nanoparticles, different synthesis by plasma of polypyrrole particles have been investigated highlighting the advantages to be carried out in gas phase without any other chemical agents except the base monomers. Spherical particles have been obtained with this process with diameter between 35 and 350 nm [13] and nanotubes with diameter of 30 nm and length between 160 nm and up to 60 μm [14]. Considering this technique of high energy synthesis, this work presents a study about the growth of titanium oxide nanoparticles synthesized with glow discharges of water and titanium tetrapropoxide ($Ti(-O-CH_2-CH_2-CH_3)_4$) vapors.

2. Synthesis

The titanium oxide particles were synthesized at 13.5 MHz with resistive coupling in a 1500 cm^3 vacuum tubular glass reactor. The reactor had stainless steel flanges and electrodes of 6.5 cm in diameter spaced 12 cm. Approximately, 0.03 g of TTP was spread on polyethylene supports, frozen in liquid nitrogen and placed inside the reactor. It was all TTP used in each synthesis. In another sealed recipient connected to the reactor, distilled water was deposited at room temperature. The plasma discharges were applied with the vapors of water and TTP that slowly unfroze and vaporized. The other conditions were: 0.6-0.8 mbar, 60-240 min and 100 W.

Depending on the electric field applied to the reactor, the particles in the plasma may have electronic density and energy up to 10^8 cm^{-3} and 15 eV, respectively [15]. In these conditions, most of TTP chemical bonds break and rearrange into other structures. The lowest energies are found in the organic bonds C-O (3.56 eV), C-C (3.6 eV) and C-H (4.3 eV) which can be the most affected by the continuous collisions with the particles in the plasma.

The breaking of molecules can produce separation of the organic and inorganic parts of TTP with the subsequent formation of Ti oxides. Thus, the result of such chemical reactions is a white powder composed of titanium oxides and residues of the TTP organic fraction.

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Table 1. Elemental analysis in %At of titanium oxide powder synthesized on polyethylene at 100 W with different reaction time. H atoms were not considered.

Element	**TTP** (%At)	**Titanium oxide powder** (% At)			
		60 min	120 min	180 min	240 min
C	70.58	17.86	22.0	15.99	24.23
O	23.52	55.10	44.27	46.94	50.32
Ti	5.89	27.04	33.72	37.07	25.44
O/Ti	4	2.04	1.31	1.27	1.98
C/Ti	12	0.66	0.65	0.43	0.95

3. Results and Discussion

3.1 Elemental Analysis

Elemental analysis of the resulting powder was obtained by X-ray energy dispersive spectroscopy (EDS) with an Oxford 7279 probe mounted on a Jeol 5900 LV scanning electron microscope. The elements analyzed were C, O and Ti. The elemental content of the powder at different reaction times is shown in Table 1. H atoms were not detected and for the same reason not considered in this analysis.

The data show that the C/Ti atomic ratio decreased from 12 in TTP to 0.43 in the powder synthesized at 180 min. In the first 120 min of reaction, C/Ti is very similar, 0.65 to 0.66, and in all cases is less than 1. This ratio indicates that the chemical reactions in the plasma separated a great part of TTP organic fraction which leaves the system, probably as small oxidized hydrocarbon molecules. The inorganic fraction containing titanium oxides remained on the substrates with some hydrocarbon residues.

The analysis also shows a decrease in the O/Ti ratio, from 4 in TTP to 1.27 in the powder synthesized at 180 min. In the shortest and longest reaction time, O/Ti is close to 2, suggesting a TiO_2 structure. These data also indicate that there are changes in the Ti-O bonds of the original TTP structure. Relations O/Ti close to 2 may result in crystalline phases of titanium oxide.

3.2 Morphology

The morphology of the powder obtained was studied with a Jeol 5900 LV scanning electron microscope. The images were taken on the polyethylene supports used in the synthesis. Figures 1-4 show different configuration of particles, there are phases of nucleation, growth and agglomeration of particles. Each micrograph has an associated particle size distribution calculated with the normal distribution equation (1)

[16]:

$$f(\phi) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\phi-\mu}{\sigma}\right)^2} \qquad (1)$$

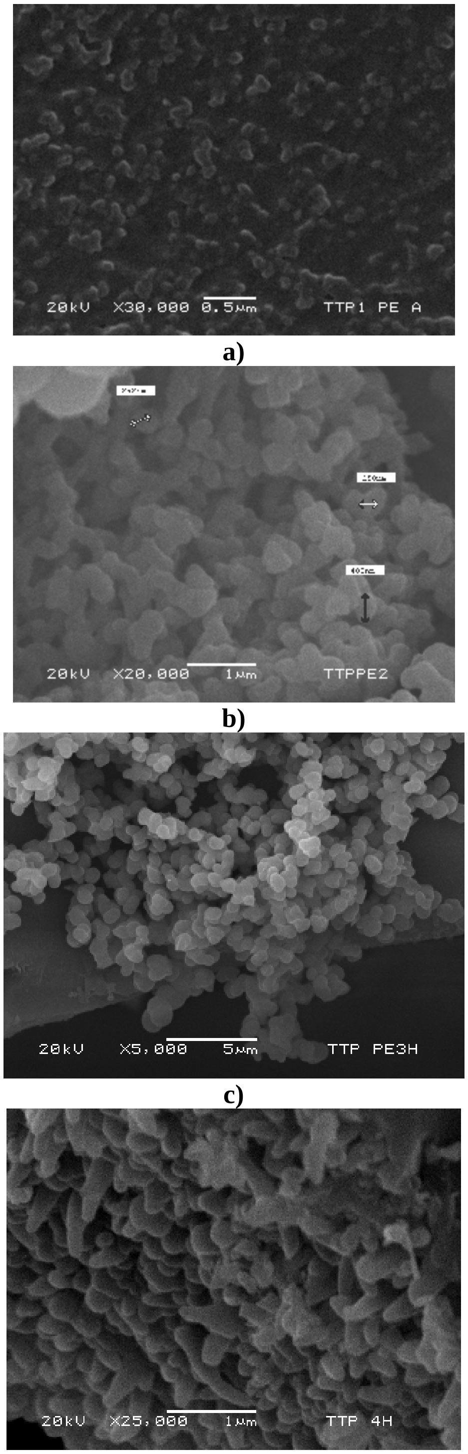
Where φ represents the particle diameter, μ the harmonic mean and σ the standard deviation. The more representative particles of each micrograph were measured with the free distribution program MeasureIT. The maximum value on each distribution corresponds to the harmonic mean.

Figure 1(a) shows the nucleation phase of particles. The synthesis time is 60 min. During this phase, the particles have various geometries with diameters from 65 to 170 nm and mean at 106.3 nm. Incipient nucleation may be due to low interaction of TTP with the high-energy particles in the plasma.

The formation of particles on the surface is shown in Figure 1(b) at 120 min of reaction. The particles have a diameter between 160 and 415 nm with mean at 281.9 nm. In this phase, the particles already have hemispherical geometry with mean diameter 2.65 times higher than the previous case. The maximum growth of particles is achieved at 180 min of reaction. Figure 1(c) show spherical particles and diameters from 470 to 1170 nm and mean at 695.8 nm.

Finally, Figure 1(d) shows agglomeration of particles with spherical and fibrous geometry. The diameters are between 140 and 300 nm with mean at 206 nm. The particle size at this phase was reduced to 0.3 times the maximum diameter. In these micrographs, the titanium oxide powder shows a fibrous morphology, suggesting that the particles are aligned in one common direction forming fibrous structures.

The growth of particle diameter is a function of reaction time with an initial stage of growth and a subsequent reduction. In the first phase, TTP bonds are modified to create different titanium oxides. However, with prolonged exposure to the plasma, the availability of TTP is reduced; but the titanium oxide particles continue reacting between them, because of the continuous collisions with the accelerated particles in the plasma, changing their morphology from spherical to fibrous profile. It is probable that the elongation of particles occurs at the expense of the comparative reduction in diameter. As discussed before, the Ti/O atomic ratio has also variations with the time of exposure to the plasma.



a) **b)** **c)** **d)**

Figure 1. Titanium oxide powder synthesized from 60 to 240 min. (a) Nucleation of particles with irregular morphology at 60 min. (b) Formation of hemispherical particles at 120 min. (c) Growth of spherical particles at 180 min. (d) Arrangement of fibrous particles with diameters between 140 and 300 nm at 240 min.

3.3 Growth of particles

Figure 2 describes the evolution of the particle diameter of this work. The insets are the associated size distribution calculated with the normal distribution equation, illustrative of the mean diameter position of each synthesis time. The tendency of mean diameters shows a two-stage growth, increase and decrease of diameter, with maximum at 180 min of synthesis and diameter of 695.9 nm.

The evolution of diameters is an expression of the morphology tendency of particles. The process is a batch synthesis, where all TTP used is deposited in the reactor from the beginning without additions. On the opposite, water, the other chemical regent used, was added constantly during the synthesis. Thus, the particles nucleate and grow continuously while TTP lasts, however, at the same time, the particles are subjected to the continuous collisions of the accelerated plasma particles, electrons and ions, which erode and rearrange the structure and morphology of the particles already formed in competitive processes that depends on the thermodynamical and electrical conditions of the synthesis.

With these processes, different diameter tendencies can be identified at any time, which is shown in Figure 2. The curves show that the mean diameter decreases after 180 min, where the erosion has more influence than the increase of diameter, perhaps because the amount of TTP has been greatly reduced after this, point. The result in general terms is that the diameter decreases after TTP reaches a low critical value. Both processes, increase and decrease of diameter, are not symmetrical because the conditions in which they occur are different. As a function of time, the growth is slightly more elongated in the growing stage, $60<t<180$, than in the decreasing of diameter.

4. Conclusions

The synthesis by plasma of titanium oxide particles with precursors such as TTP and water indicates that the ions and electrons accelerated by the electric field can change practically all TTP chemical bonds. The effectiveness of chemical reactions can be seen in the C/Ti atomic ratio which changes from 12 in TTP to 0.43-0.95 in the final titanium oxide powder, more than 90% of reduction in the organic phase. At 100 W, the resulting compounds have atomic O/Ti ratio between 2.04 and 1.27. Some varieties of TiO_2 crystalline phases have O/Ti ratio close to 2.

The study of particle growth indicates a parabolic tendency as a function of reaction time. Given that the synthesis is carried out on discrete processes where the initial amount of TTP decreases as it reacts, there is a point of maximum particle growth in the evolution, and after that, the precursor reduction decreases the growth of particles. The maximum particle size with a harmonic mean of 695.8 nm and hemispherical morphology was presented at 180 min of reaction.

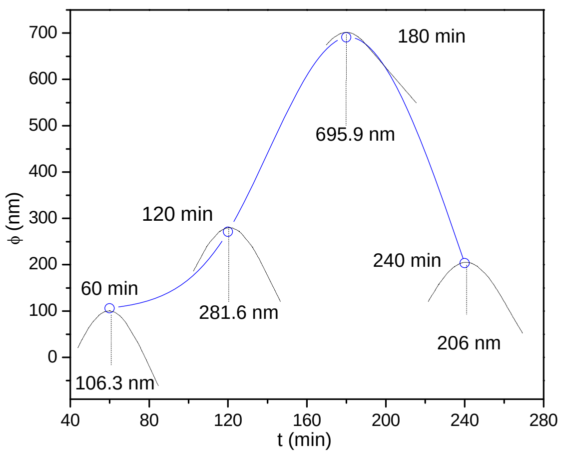


Figure 2. Particle diameter as a function of synthesis time.

The formation and agglomeration of particles with spherical and fibrous geometry with a mean diameter of 206 nm was found at 240 min of synthesis.

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References

[1]. X. Fan, L. Lin, B. P. Messersmith. Composites Science and Technology. 66, 1195 (2006).

[2]. H. Yang , K. Zhang, R. Shi, X. Li, X. Dong, Y. Yu., Journal of Alloys and Compounds. 41, 302 (2006).

[3]. S. Pavasupree, S. Ngamsinlapasathian, M. Nakajima, Y. Suzuki, S. Yoshikawa. Journal of Photochemistry and Photobiology A: Chemistry. 184, 163 (2006).

[4]. J. Aguado, R. van Grieken, M.J. López-Muñoz and J. Marugán. Catalysis Today. 75, 95 (2002).

[5]. F. Fresno, J. M. Coronado, D. Tudela, J. Soria. Applied Catalysis B: Environmental. 55 (3), 159 (2005).

[6]. D.L. Liao, G.S.Wu, B.Q. Liao. Colloids and Surfaces A: Physicochem. Eng. Aspects. 348, 270 (2009).

[7]. B. F. Cottam, S. Krishnadasan, A. J. deMello, John C. deMello and M. S. P. Shaffer. The Royal Society of Chemistry. 7, 167 (2007).

[8]. R. Szabova, L. Cernákova, M. Wolfová, M. Cernák. Acta Chimica. Slovaca. 2(1), 70 (2009).

[9]. X. Chen**,** M. Schriver**,** T. Suen and S. S. Mao**.** Thin Solid Films. 515(4), 8511(2007).

[10]. S. Pavasupree**,** Y. Suzuki**,** S. Yoshikawa and R. Kawahata**.** J. Solid State Chemistry. 178(10), 3110(2005).

[11]. S. Pavasupree, S. Ngamsinlapasathian, M. Nakajima, Y. Susuki, S. Yoshikawa. J. Photochem. Photobiol. A: Chem. 184, 163 (2006).

[12]. J. Ani, S. Savithri, G. Surender. Aerosol and Air Quality Research. 5, 1(2005).

[13]. G.J. Cruz, M.G. Olayo, O.G López, L.M. Gómez, J. Morales, R. Olayo. Polymer. 51, 4314 (2010).

[14]. R. Asmatulu, A. Karthikeyan, D. C. Bell, S. Ramanathana and M. J. Aziz. Journal of Materials Science. 44, 4613 (2009).

[15]. M.G. Olayo, J. Morales, G.J. Cruz, S.R. Barocio, R. Olayo. Journal of Polymer Science, Part B: Polymer Physics. 41, 1501 (2003).

[16]. W. Li, S. Ismat, M. Sung, C.P. Huang. J. Vac. Sci. Technol. B. **20**, 2303 (2002).