INFLUENȚA CONDIȚIILOR DE OBȚINERE ASUPRA STRUCTURII ŞI MORFOLOGIEI NANOPULBERILOR DE ANATAS

THE INFLUENCE OF OBTAINING CONDITIONS UPON THE STRUCTURE AND MORPHOLOGY OF ANATAS NANOPOWDERS

GEORGIANA-LAURA PARASCHIV, ŞTEFANIA STOLERIU[*]
Universitatea POLITEHNICA Bucureşti, Str. G. Polizu nr. 1, S1, 011061, Bucureşti, România

Nanocrystalline TiO_2 semiconductor represents the ideal photocatalyst due to its high photocatalytic reactivity, chemical stability, non-toxicity, low price, availability, and redox efficiency. However, only the optoelectronic properties of anatase structure make it adequate for its useage as a photocatalytic material able to oxidize many organic and inorganic molecules in the presence of near-UV radiation.

In order to obtain anatase TiO_2-polymorph nanoparticles, four methods were studied, all using titanium (IV) butoxide as precursor alkoxide. Method A was the simple precipitation method, and method B involved a sol-gel route. The methods C and D were derived from sol-gel technique: C - involves obtaining an yellow gel; and D – where water was not added for hydrolysis.

The obtained powders were calcinated and characterized using specific methods: X-ray diffraction, high resolution transmission electron microscopy-HRTEM, differential thermal analysis and FT-IR spectroscopy.

Materialele semiconductoare nanocristaline pe bază de TiO_2 reprezintă fotocatalizatorul ideal datorită reactivității fotocatalitic mari, a stabilității chimice, non-toxicității, prețului scăzut, disponibilității şi eficienței redox. Cu toate acestea, proprietățile optoelectronice ale structurii anatasului, îl face adecvat pentru utilizarea sa ca material fotocatalitic capabil de a oxida multe molecule organice şi anorganice, în prezența radiațiilor UV-A.

În scopul de a obține nanopulberilor de anatas, au fost studiate patru metode, toate folosind butoxid de titan (IV) ca precursor. Metoda a fost o metodă simplă de precipitare, iar metoda B a implicat un proces sol-gel. Metodele C şi D au fost derivate din tehnica sol-gel: C - presupune obținerea unui gel galben şi D - în care nu a fost adăugată apă pentru hidroliză.

Pulberile obținute au fost calcinate şi apoi caracterizate prin metode specifice: difracție de raze X, microscopie electronică de transmisie de înaltă rezoluție - HRTEM, analiza termică diferențială şi spectroscopie FT-IR.

Keywords: *anatase, nanoparticles, synthesis methods, titanium (IV) butoxide*

1. Introduction

Nanocrystalline TiO_2 semiconductor particles present interest due to their special properties and potential technological applications, which are based on photocatalysis process. Following countless research studies, it was shown that TiO_2 is the semiconductor which displays the most efficient photocatalytic properties, thus explaining its use in a wide range of applications: in the field of building materials with special properties (such as photocatalytic cement [1,2], glass [3], paint [4,5] etc.), gas sensors, MEMS devices (microelectronic mechanical systems) [6,7], solar cells (dye-sensitize) [8], supercapacitors [9] and information storage devices [10]. Nanocrystalline TiO_2 semiconductor represents the ideal photocatalyst due to its high photocatalytic reactivity, chemical stability, non-toxicity, low price, availability, and redox efficiency [11, 12].

There are 3 types of TiO_2 crystalline structures: anatase, rutile and brookite. In each structural model, the titanium ion is surrounded by six oxygen atoms, which in turn, are linked to three titanium atoms. Anatase and rutile have tetragonal crystal systems, while brookite is orthorhombic. However, only the optoelectronic properties of anatase structure make it adequate for its use as a photocatalytic material. On one hand, the anatase band gap is quite wide (Eg = 3.23 eV), and, on the other hand, the oxidation potential of the valence band is relatively large, equal to 3.1 eV (at pH=0). Both anatase-type semiconductor characteristics led to the conclusion that many organic and inorganic molecules can be oxidized in the presence of TiO_2 and UV-A radiation [13].

It has been observed the manifestation of new physical and chemical properties with the decreasing particle size until it reaches the nanometric scale. The material properties also can vary, depending on the shape of nanometric particles. The unique properties exhibited by

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[*] Autor corespondent/*Corresponding author*,
Tel.: +4021 402 39 97, e-mail: s stoleriu@yahoo.com

nanomaterials may be due to the movement of electrons and holes in semiconductor nanoparticles, motion governed by the phenomenon of quantum constraint, and the transport properties, correlated with photons and phonons, are highly affected by the size and geometry of materials. The specific surface area and surface:volume ratio increases dramatically with the decreasing of particle size. The high surface area provided by small particle size is advantageous to multiple TiO_2-based devices/ materials, facilitating the reaction/interaction between the devices and the interaction environment, which generally occur on the surface or at the interface and dependent greatly on the contact surface between these two.

Therefore, the performances of TiO_2-based devices/materials are highly influenced by the size of the TiO_2 structure units, apparently at the nanoscale [14].

2. Experimental methods used for synthesis of TiO_2 nanopowders

In order to obtain anatase TiO_2 nanoparticles, four methods were studied, all using titanium (IV) butoxide as precursor alkoxide.

2.1. METHOD A: precipitation method

One of the easiest ways to obtain dispersed powders of metal oxides, including TiO_2, is precipitation method. Research studies [13] exhibits that the minimal size of primary particles is independent of the precipitating agent nature. Depending on the precipitation conditions, primary particles unite to form clusters of different sizes. The aggregation degree depends on many factors and can be controlled via precipitation conditions. Varying temperature, time and pH of the environment, titanium dioxide can be synthesized with different phase compositions. In addition, an important factor in controlling the hydrolysis rate is water.

Precipitation method involves a combination of obtaining a precipitate and its drying process. Precipitation occurs through hydrolysis processes, the reactions starting from titanium (IV) butoxide are as follows [14]:

$$Ti(O(CH_2)_3CH_3)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4CH_3(CH_2)OH \quad (1)$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (2)$$

In order to prepare the solution, titanium (IV) butoxide ($Ti(OC_4H_9)_4$, (97%, Aldrich Chem.) was used as starting material. The reaction was necessary to take place in an acid environment, so HCl (conc. 38%) was added dropwise into titanium butoxide until the solution reached a pH~2. According to the reactions to obtain TiO_2, the molar ratio of titanium butoxide:distilled water was respected, being 1:4, adding distilled water under continuous stirring using a magnetic stirrer. In the presence of water, the alkoxide hydrolyzes, forming a white precipitate. After adding the entire amount of water, the precipitate obtained was left to dry at 80°C for 24 hours, then calcinated at a temperature of 350°C for 3 hours.

2.2. METHOD B: sol-gel method

Sol-gel method is probably the most used technique for the synthesis of TiO_2 nanoparticles. Sol-gel method is based on the hydrolysis reaction of an alkoxide or halide precursor with a subsequent condensation of the inorganic component. The formation of TiO_2 from a titanium alkoxide (IV) takes place by acidic hydrolysis followed by polycondensation of the alkoxide, according to the reactions [15]:

$$Ti(OR)_4 + H_2O \xrightarrow{H^+} Ti(OR)_3(OH) + ROH \quad (3)$$

$$Ti(OR)_4 + Ti(OR)_3(OH) \rightarrow Ti_2O(OR)_6 + ROH \quad (4)$$

Polycondensation is stopped by the addition of two water molecules:

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH \quad (5)$$

Within this method of TiO_2 synthesis, titanium (IV) butoxide (97%) was used as precursor, isopropyl alcohol (99.8%, Fluka) as solvent, in order for the hydrolysis reaction to take place distilled water was added, and as chelating agent, the organic polymer polyethylene glycol (PEG) with molecular weight=3000. The ratio between titanium butoxide:(alcohol+water) was considered to be 1:4, those 4 parts of liquid being divided as follows: 3 parts isopropyl alcohol and 1 distilled water. The precursor was introduced into the reaction vessel, adding 1 part isopropyl alcohol under continuous stirring for 10 minutes. While mixing the chelating agent (PEG) was slowly introduced into this transparent solution in a proportion of 2%, the ratio of titanium butoxide:PEG being 1:0.02and heated up to 200°C. After a complete dissolving of PEG into the solution, a mixture of 1 part distilled water and the 2 remaining parts of isopropyl alcohol were added dropwise, simultaneously adding HCl (38%) to obtain a solution of pH = 2-3. It was observed the occurrence of some precipitate in the transparent solution with the addition of water-alcohol mixture, but the precipitate dissolved almost immediately. In the presence of constant temperature (200°C), under continuous stirring, a very rapid process of gelification took place. The obtained gel was left to age for 24 h, after which it was dried for 24 h at 80°C and calcined for 3 h at 350°C.

2.3. METHOD C: "yellow gel" method

This method is a simple, effective and feasible route to obtain TiO_2 nanopowders containing mainly anatase or even some thin films deposited on various substrates, using a titanium peroxo complex as substance with titanium intake. The advantages of this method are: simplicity and ease of control, and if chosen to obtain thin films, is easily fixed on substrates with complex surfaces or with a high specific surface [16].

To prepare the gel, titanium butoxide (97%) was used as alkoxide, which was hydrolyzed with distilled water, the resulting precipitate - titanium hydroxide, was separated by decantation and washed thoroughly with water until the alcohol generated during the alkoxide hydrolysis was completely removed. Then the precipitate was dissolved in hydrogen peroxide (30%), under vigorous stirring, in order to obtain a transparent orange sol – titanium peroxo complex. After a while, *a bright yellow gel* is obtained. The ratio of titanium butoxide:distilled water:hydrogen peroxide used in this experiment was equal to 0.048:1:0.75. The obtained gel was left to age for 24 h, then was dried at 80°C for a period of 40 hours, followed by a calcination process conducted for 3 h at 350°C.

2.4. METHOD D: method B modified

This method is actually derivated from method B (sol-gel method), in which water was not added for hydrolysis and after 4 hours the solution, kept at room temperature, gelified in the reaction vessel.

Explanations for this phenomenon are given in [17], which state that for low concentrations of water, hydrolysis rate is low and the excess of titanium alkoxide in solvent favors the development of Ti-O-Ti chains through alkoxylation mechanism.

This method is similar to sol-gel method described above, so, as alkoxide precursor, titanium (IV) butoxide (97%) is also used, which is mixed with isopropyl alcohol (99.8%), the molar ratio between the two being butoxide:alcohol = 1:1. The solution is kept under stirring for 30 minutes, during which the solution is heated up to a temperature of 200°C. The chelating agent PEG (molar ratio of butoxide Ti:PEG = 1:0.04) was slowly added, dissolving in the presence of temperature and continuous stirring. After the stage of PEG dissolving had been reached, isopropyl alcohol was added dropwise, considering the final ratio between butoxide:alcohol to be equal to 1:4. HCl (38%) was added to reduce the solution's pH to a value of 2-3. After 4 hours at room temperature, it looked similar to a white viscous emulsion. It was dried for 48 hours at 80°C, followed by calcination process for 3 hours at 350°C.

3. Characterization of TiO_2 nanoparticles

All powders obtained and calcined were subject to a series of tests, these being: X-ray diffraction (Shimadzu XRD 6000 X-ray diffractometer), high-resolution transmission electron microscopy (HRTEM, Tecnica G^2 F30 S-TWIN), ATD differential thermal analysis (Analyzer Shimadzu DTA 50) and FT-IR spectroscopy (Shimadzu FTIR 8400 Spectrophotometer); in the case of thermal analysis, there were analyzed both dry samples and non-calcined.

3.1. Thermal methods of analysis

Figure 1 shows the DTA, TG and DTG curves of dry powders obtained by the methods A, B and C.

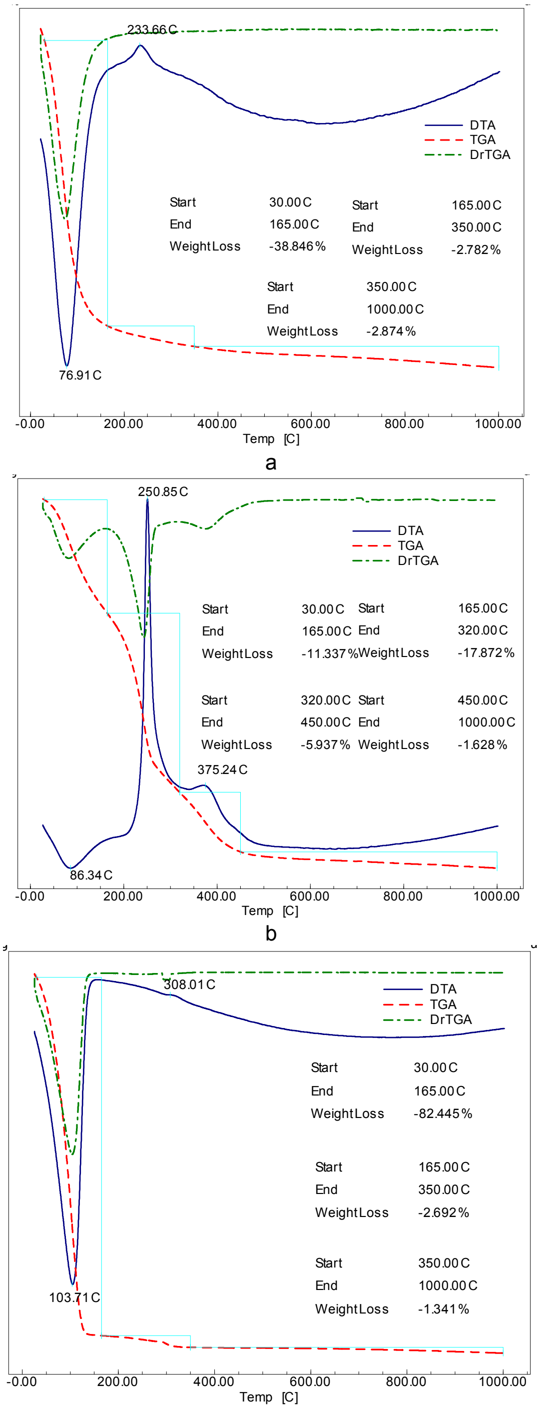


Fig. 1 - Complex thermal analysis of powders obtained by methods A (a), B (b) and C (c)/ *Analizele termice complexe ale pulberilor obținute prin metodele A (a), B (b) şi C (c).*

In the case of the powder obtained by method A, it can be seen that at temperatures up to 100°C almost the entire weight loss is registred, because in this range several processes take place: not only physical evaporation, but also the decomposition of titanium hydroxide generated during the hydrolysis reaction; the slightly exothermic effect recorded at 234°C is due to combustion of organic part of the precursor of titanium used.

Same applies for powder obtained by method C.

For the powder obtained by sol-gel - method B, the effects are:

- endothermic effect at 87°C, due to dehydration of physically bound water;
- the strong exothermic effect from 250°C belongs to combustion of the titanium precursor organic part, but especially to burning of PEG used for chelation;
- the less intense exothermic effect recorded at 374°C is accompanied by weight loss and therefore can be attributed to the complete combustion of the organic parts. It also corresponds to the temperature of anatase crystallization from amorphous phase.

Based on this analysis, it was decided that the calcination temperature to be 350°C.

3.2. X-ray diffraction analysis

After the samples were calcined, they were subject to X-ray diffraction. The obtained spectra are shown in Figure 2.

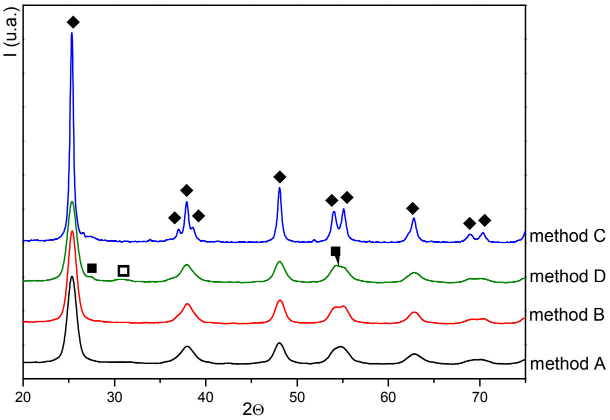


Fig. 2 - XRD spectra of nanopowders synthesized by methods A, B, C, D
(◆ – anatase; ■ – rutile; ☐ – brookite)
Spectrele de difracţie al razelor X ale nanopulberilor obţinute prin metodele A, B, C, D (◆ – anatas; ■ – rutil; ☐ – brookit).

In all cases of calcined powders obtained by all four methods, diffraction effects specific anatase were detected. The powder obtained by method D is slightly contaminated by the presence of rutile and brookite. It was also noted that through method C well crystallized powders are obtained.

3.3. FT-IR spectrometry

Figure 3 shows the infrared absorption spectra of the calcined powders obtained by methods A and C.

IR absorption spectra for both calcined powders show only characteristic bands of Ti-O–Ti bonds (the wide band between 500 and 1500 cm^{-1}, 1645 cm^{-1}) and specific anatase octahedrals $[TiO_6]^{8-}$ bonds (470 cm^{-1}) [18], without any other organic and inorganic contaminations. It should be, also, noted the specific bands of adsorbed water and OH bonds (corresponding wavelength of 3500cm^{-1} and 1630 cm^{-1}).

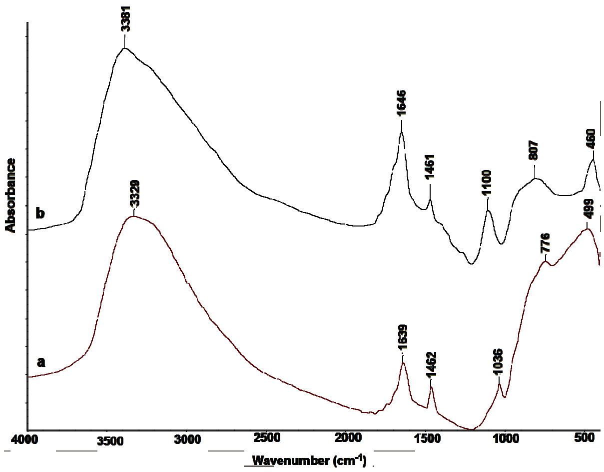


Fig. 3 - FT-IR absorption spectra of calcined nanopowders synthesized by methods A (a) and C (b)/ *Spectrele de absorbţie FT-IR ale nanopulberilor calcinate obţinute prin metodele A (a) şi C (b).*

3.4. Apparent density of nanopowders

Measurements were made to determine the powders density after calcination in order to observe the density variation depending on the method used to obtain TiO_2 nanopowders. Experimental determinations were made using the most common method for determining the powders density, which is pycnometer method.

Table 1

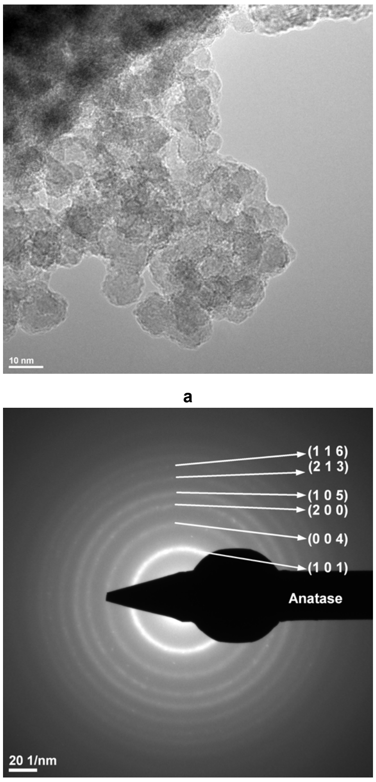
Apparent densities for obtained TiO_2 nanopowders
Densităţile aparente ale nanopulberilor de TiO_2 obţinute

Polymorph form *Forma polimorfă*	Theoretical density *Densitatea teoretică* (g/cm^3) [19]
Anatase	3.79 – 3.97
Rutile	4.23 – 4.25
Brookite	4.08 – 4.18
Synthesis method *Metoda de sinteză*	Apparent density *Densitatea aparentă* (g/cm^3)
A	3.78
B	3.98
C	3.93
D	3.68

All values obtained for the apparent density induces the idea that they tend to be closer to the value of anatase mineralogical form, instead of other polymorphic forms of TiO_2.

3.5. Transmission electron microscopy analysis

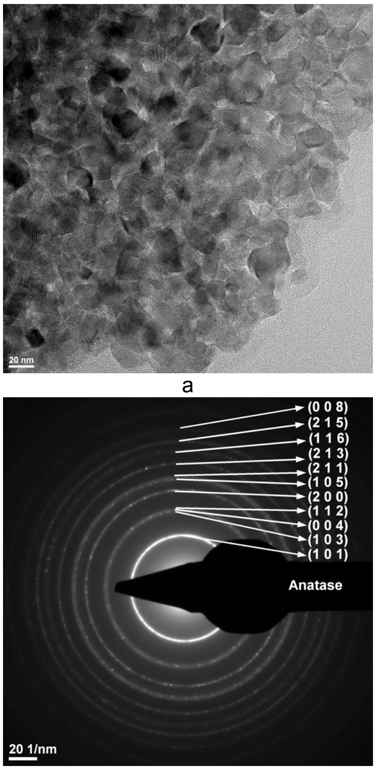
The transmission electron microscopy images give indisputable evidence that the obtained powders are nano-sized. The images for powders synthesized by considered methods are shown in the following figures.



a

b

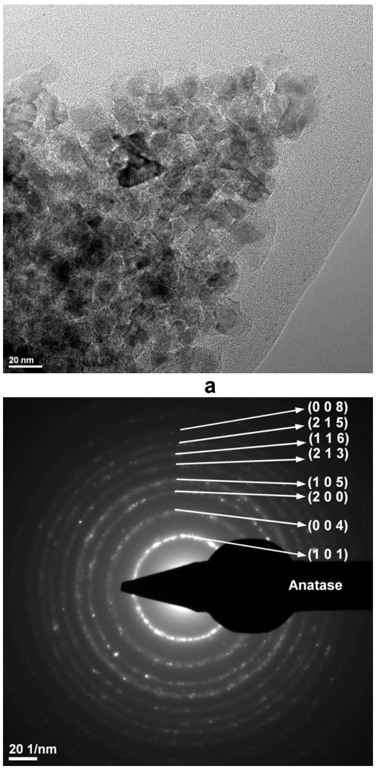
Fig. 4 - TEM images for calcined powder obtained by method A: a. bright field transmission electron microscopy; b. selected area electron diffraction./ *Imagini TEM ale pulberii calcinate obținute prin metoda A: a. imagine TEM în câmp luminos; b. difracție de electroni pe arie selectată.*



a

b

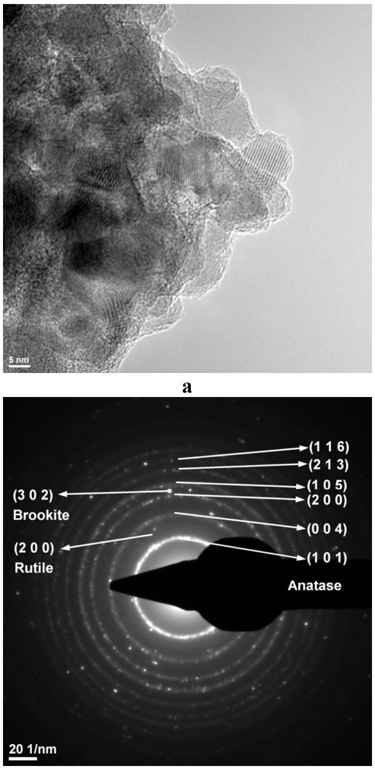
Fig. 5 - TEM images for calcined powder obtained by method B: a. bright field transmission electron microscopy; b. selected area electron diffraction/ *Imagini TEM ale pulberii calcinate obținute prin metoda B: a. imagine TEM în câmp luminos; b. difracție de electroni pe arie selectată.*



a

b

Fig. 6 - TEM images for calcined powder obtained by method C:a. bright field transmission electron microscopy; b. selected area electron diffraction / *Imagini TEM ale pulberii calcinate obținute prin metoda C: a. imagine TEM în câmp luminos; b. difracție de electroni pe arie selectată.*



a

b

Fig. 7- TEM images for calcined powder obtained by method D: a. bright field transmission electron microscopy; b. selected area electron diffraction / *Imagini TEM ale pulberii calcinate obținute prin metoda D: a. imagine TEM în câmp luminos; b. difracție de electroni pe arie selectată.*

TEM micrographs corresponding to figures 4 -7 attest the obtaining of nanopowders with a particle size less than 10 nm in the case of method A (fig. 4a) and 20 nm in the case of methods B (fig. 5a) and C (fig. 6a).

The selected-area diffraction pattern for obtained samplea indexes to anatase, in agreement with the X-ray diffraction data. In Figure 7b, the SAED patterns of TiO_2 powders shows spotty ring patterns of anatase with additional diffraction spots of second phases, revealing their well crystalline. On the other hand, the SAED patterns of TiO_2 powder obtained through method A (Figure 4b) shows that the brightness and intensity of anatase rings are weak, so the powder is poorly crystallized and partly amorphous.

4. Conclusions

TiO_2 nanoparticles were successfully obtained by four methods of synthesis, using titanium (IV) butoxide as an alkoxide precursor. The first two methods (A and B) of synthesis have the following advantages: simple, feasible, does not require high temperatures and the TiO_2 nanopowders obtained have a high degree of crystallinity and purity.

In terms of phase composition, the X-ray spectra shows that in all methods used the TiO_2 nanoparticles are composed of anatase polymorphic form, except in the case of method D, which is contaminated by the presence of rutile. The nanometric size, crystallinity degree and purity are confirmed by transmission electrons microscopy analysis performed on all powders, obtaining even particle sizes of 5 nm, in the case of precipitation method.

Therefore, it was concluded that the most effective methods of synthesis of TiO_2 powders, which ensures the obtaining of nanocrystalline particles that contain anatase phase necessary to achieve future photocatalytic properties, are precipitation and sol-gel methods.

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