Effects of ultrasound/microwave irradiation on the sol-gel synthesis of titanium dioxide nanoparticles for photocatalytic application

Y Zarazua-Aguilar1*, SP Paredes-Carrera1, JC Sánchez-Ochoa1, JR Avendaño-Gómez2, SO Flores-Valle3

1 Laboratorio de Nanomateriales Sustentables ESIQIE, Instituto Politecnico Nacional, Zacatenco, D.F, CP 07738 Mexico. E-mail: yozara1986@gmail.com
2 Laboratorio de Ingeniería Ambiental, ESIQIE, Instituto Politecnico Nacional, Zacatenco, D.F, CP 07738, Mexico
3 Laboratorio de Química Verde, ESIQIE, Instituto Politecnico Nacional, Zacatenco, D.F, CP 07738, Mexico

ABSTRACT

TiO2 nanoparticles were synthesized by the sol-gel method with the purpose of optimizing their morphological and structural properties, for their application in photocatalysis by varying the thermal treatment in the crystallization stage. Each sample was prepared according to the case with microwave irradiation (MO), ultrasound (US), combined mode (microwave-ultrasound (MC)) or conventional method (reflux), where the MC method has not been reported. It was found that the optical (edge energy (Eg)), textural and morphological properties depend on the type of irradiation during the crystallization stage. The SEM micrograms (scanning electron microscopy) showed two morphologies, one in the form of monoliths and the other as aggregates of lobular particles. In the case of MO and reflux, it is made up of aggregates of lobular particles, for US in the form of monoliths and finally for MC, the dominant morphology is due to the effect of US. For the evaluation in photocatalysis, it was observed in the samples studied that the higher the percentage of anatase phase, surface area, volume and pore size, all at the same Eg value, the greater the photodegradation of methyl orange. Therefore, TiO2 synthesized by the combined MC method was the best material obtained for photodegradation.

Keywords: TiO2; Sol-Gel; Microwave; Ultrasound; Reflux

1. Introduction

Currently, the synthesis of nanomaterials is one of the most studied branches within nanosciences, by reducing the particle size down to nanometer scale (1–100 nm) the physical and chemical properties are modified with respect to their macrometer scale counterpart[9]; since the movement of electrons is limited by the dimensions of each material, due to the high surface-to-volume ratio, which makes these materials have a large amount of atoms on the surface to interact with each other[2]. Based on the above, nanomaterials have wide applications in the area of catalysis and photocatalysis[3]. Specifically, TiO2 due to its photoelectric properties, is widely used in the area of photocatalysis[4,5]. It can be found naturally in three crystal structures (Figure 1): anatase (tetragonal), rutile (tetragonal) and brookite (rhombohedral); where the most stable phase is the rutile phase, however, anatase is the one with the most photoactive phase, due to the fact that in its crystallographic structure it contains a greater amount of surface oxygen susceptible to form OH radicals, in addition to retarding the recombination of electron-hole pairs[7]. These phases present an edge energy of 3.0
eV and 3.2 eV respectively, being photoactive with UV light\cite{8,9}. Therefore, new synthesis methods have been sought to increase the percentage of anatase phase, as well as to improve the textural, morphological and optical properties of TiO$_2$ to optimize the surface-to-volume ratio and thus increase the efficiency of the process. It has been observed that experimental conditions during synthesis such as: precursors, synthesis times and heat treatment result in mesoporous particles with different specific areas and various morphologies: cubic, cylindrical, spherical and needle-like\cite{10-12}. Previous work shows that in order for the anatase phase to be favored during synthesis, methods such as hydrothermal, microemulsion, inert gas condensation and sol-gel have been employed\cite{13}.

The sol-gel process is one of the most widely used methods to synthesize TiO$_2$, basically consisting of the formation of a colloidal suspension (sol) and its subsequent gelation formed by networks or chains of disordered atoms (gel). The resulting gel is subjected to heat treatment for the formation of crystalline structures. The crystallization stage is carried out by conventional heating, such as reflux (T = 80 °C) and autoclaving (T = 120 °C). These methods have the disadvantage that they are expensive due to energy consumption and require long synthesis times, which are between 2 and 72 h\cite{14,15}. For this study, the use of microwave and ultrasound irradiation methods was proposed. These irradiation methods present advantages over conventional treatments, since the heating rate is faster, the crystallization kinetics is accelerated and can promote the formation of new metastable phases\cite{16}. In addition, they allow the formation of particles of different sizes with different morphologies and textures depending on the type, time and power of irradiation (microwave-ultrasound)\cite{17-19}.

In this work a study of the morphological, optical and textural properties of TiO$_2$ synthesized by the sol-gel method was carried out, using microwave irradiation, ultrasound and combined mode (microwave-ultrasound) during the crystallization stage according to the sample to be prepared. The combined mode has not been reported in the synthesis of TiO$_2$, however, it has been employed in the synthesis of other materials such as copper nanoparticles, where the synergistic effect of microwaves and ultrasound was observed\cite{20}.

## 2. Experiment

### 2.1 Synthesis

TiO$_2$ nanoparticles were prepared by sol-gel method assisted by microwave irradiation (MO), ultrasound (US), combined mode (microwave-ultrasound (MC)) and conventional heating (reflux (C)) respectively. First, ethyl alcohol (Fermont, 96°) was added with distilled water, then hydrochloric acid (Fermont, 37%) was added as hydrolysis precursor, titanium butoxide (Aldrich, 97%) was added keeping the system under stirring, each of the above mixtures was given different heat treatment as follows:

- **a) Conventional heating (reflux).** The mixture was kept under reflux at T = 80 °C for 2 h, the sample obtained was designated as TiO$_2$-C\cite{21}.

- **b) Ultrasound irradiation.** The mixture was placed in a microwave, ultrasound and cooperative mode reactor model SBL CW-2000A, with a volume 500 mL for 5 min in ultrasound operation mode at a power of 50 W and a frequency of 40 KHz, this sample was named TiO$_2$-US.

- **c) Microwave irradiation.** This mixture was kept for 5 min in the mentioned reactor working with a power of 800 W and 2450 Hz, this sample was named TiO$_2$-MO.

- **d) Combined mode (MC) (microwave-ultrasound).** For this mixture the operation modes of both irradiation methods were combined simultaneously, using the same reactor at the same conditions, this sample was identified as TiO$_2$-MC. In all cases at the end of the reaction the samples were dried at 70 °C for 12 h, then calcined in a Vulcan A-130 muffle at 400 °C for 4 h.

### 2.2 Characterization

![Figure 1. Crystalline structures of TiO$_2$.](image)
The synthesized materials were characterized by:
• X-ray diffraction (Rigaku diffractometer model miniflex 600 with CuK α = 1.541 Å radiation) to identify the crystallographic phases, the crystal size was determined with the Scherrer equation and the Rietveld method was used to determine the lattice parameters and the percentage of phases present in each sample.
• Scanning electron microscopy (Quanta 3D FEI brand) was used to determine the morphological properties.
• Nitrogen physisorption to know the textural properties such as specific area, the BET (Brunauer-EmmetTeller) method was used, pore size and volume, at 77 °K, the measurement was made in a Micromeritics ASAP 2020 equipment, which according to the manual has an uncertainty of ±6 m²/g.

2.3 Evaluation

To evaluate the efficiency of the photocatalysts, a solution of methyl orange was prepared at a concentration of 5 ppm, with a catalyst ratio of 1 g/L and an equilibration time of 120 min.

The process was carried out in 5 mL vials in a luz-Chem carousel photoreactor, each sample was read in duplicate, adding to each tube the proportional part to have 1 g of catalyst per liter of methyl orange solution.

The vials were initially given an adsorption time of 15 min, and the amount of adsorbed contaminant was quantified by UV-Vis spectroscopy. The system was then irradiated with a UV lamp at a λ = 365 nm for 105 min, taking aliquots in duplicate every 15 min to obtain the photodegradation profile. To quantify the amount of photodegraded and adsorbed methyl orange, a Perkin Elmer Lambda XLS UV/Vis spectrophotometer was used.

3. Results and discussion

The Figure 2 shows the X-ray diffraction patterns of the synthesized TiO₂ samples.

It can be observed that in all cases characteristic crystalline structures for the anatase phase were obtained, according to the JCPD 21-1272 card the peaks correspond to the planes (101), (103), (004), (112), (111), (211), (204), (220) and (215), whose reflections at 2θ are 26, 32, 38, 40, 48, 54, 63, 70 and 78° respectively. Except for the sample prepared with microwave TiO₂-MO, the signal attributed to the brookite phase is observed in the (121) plane at 2θ = 32° according to the 29-1360 card. None of the synthesized materials present the signals attributed to the rutile phase based on the JCPD 21-1276 card.

It can be inferred that the crystallinity of the materials varies depending on the thermal treatment at the crystallization stage during the synthesis. In this case the most crystalline sample was the sample synthesized by microwaves and in descending order the samples: TiO₂-C, TiO₂-MC and TiO₂-US. In this case, microwaves allow the growth and arrangement of crystals in greater proportion with respect to the other techniques, since after nucleation during the crystallization process, the electric and magnetic fields are aligned to the dipoles of the species within the reaction, allowing their growth and arrangement gradually\[22\]. In the case of the sample synthesized by ultrasound, the cavitation effect prevents crystal growth\[23\]. As for the sample synthesized by combined mode (MO-US), it presented an intermediate behavior in terms of crystallinity, since in this case the effects of each irradiation mode were combined.

The crystal size values for the synthesized samples, as determined by the Scherrer equation, are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>β (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-MO</td>
<td>6.9</td>
</tr>
<tr>
<td>TiO₂-US</td>
<td>4.6</td>
</tr>
<tr>
<td>TiO₂-MC</td>
<td>5.9</td>
</tr>
<tr>
<td>TiO₂-C</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Figure 2. X-ray diffractograms of synthesized TiO₂, A = anatase, R = rutile and B = brookite.

Table 1. Crystal size
where $D$ is the crystal size, $\lambda$ is the X-ray wavelength (1.5401 nm), $B(2\theta)$ is the peak width at half maximum height and $\theta$ is the Bragg angle\cite{24}.

All the materials fall in the 1-100nm range, so they can be considered as nanocrystalline solids. It is also observed that the synthesis method is dependent on the crystal size, where the samples synthesized by MO, US and MC, are smaller than those presented by the conventional TiO$_2$-C sample synthesized at reflux. Which could favor the photocatalytic activity, since it has been reported that the anatase phase of TiO$_2$ with small crystal size has higher photocatalytic activity as reported by Xue\cite{25}, coupled with the apparent absence of the rutile phase. It is worth mentioning that the sample synthesized by MO is larger by 2.3 nm compared to that synthesized by US and by the combined MO-US method an intermediate size is presented.

The percentages of the phases present by the Rietveld method were calculated using the X’Pert High Score Plus program, based on the XRD (Table 2) and the lattice parameters for the anatase phase (Table 3) of the synthesized samples.

In the previous Table it can be seen that in the synthesized samples the anatase phase predominates, followed by brookite and in a lower percentage the rutile phase which was not detected by XRD. It is observed that the percentages of the phases present vary depending on the preparation technique during the crystallization stage, being the sample with the highest percentage of anatase the one synthesized by microwave, followed by the combined mode (MC), US and conventional (re-flux).

In the case of parameters $a$ and $b$ (Table 3), they are practically the same for all the synthesized samples, with a small variation of parameter $c$ of 0.2 Å. Therefore, the synthesis method does not influence the unit cell arrangement.

The preparation method (MO, US, and MC) modifies the crystal size, crystallinity, as well as the percentages of anatase, rutile and brookite in the synthesized samples. It is also observed that the lattice parameters are not modified, indicating that the chemical composition is independent of the synthesis methods.

The Table 4 presents the specific surface area calculated by the BET method, volume and pore size, obtained by the Halenda method of the titanium oxides considered in this study.

In general the specific surface areas obtained are between 62–93 m$^2$/g; exceeding the specific surface area of TiO$_2$-P25 (80% anatase and 20% rutile) whose value is 56 m$^2$/g\cite{26}. Regarding the pore size and volume it can be observed, that they are also related to the irradiation method during the synthesis. Where the sample with the largest area and porosity resulted the TiO$_2$-MC sample synthesized by combined MC method.

Figure 3 presents the adsorption isotherms obtained for the synthesized materials.

In all cases, isotherms corresponding to type IV were obtained, characteristic of mesoporous materials with $H_2$ type histoses cycle, which indicates that the porosity corresponds to cylindrical channels, formed by agglomerated particles of different sizes or with non-uniform shapes\cite{27}. There is a variation in the filling volumes according to the surface area values (Table 4), which indicates the different adsorption capacity of the materials.

Figure 4 shows the scanning electron micrographs at 5,000X and 50,000X for the TiO$_2$-MO sample, synthesized by the sol-gel method with mi-

<table>
<thead>
<tr>
<th>Table 2. Phase percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>TiO$_2$-MO</td>
</tr>
<tr>
<td>TiO$_2$-US</td>
</tr>
<tr>
<td>TiO$_2$-MC</td>
</tr>
<tr>
<td>TiO$_2$-C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3. Network parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>TiO$_2$-MO</td>
</tr>
<tr>
<td>TiO$_2$-US</td>
</tr>
<tr>
<td>TiO$_2$-MC</td>
</tr>
<tr>
<td>TiO$_2$-C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4. Textural properties of TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET sample (m$^2$/g)</strong></td>
</tr>
<tr>
<td>TiO$_2$-MO</td>
</tr>
<tr>
<td>TiO$_2$-US</td>
</tr>
<tr>
<td>TiO$_2$-MC</td>
</tr>
<tr>
<td>TiO$_2$-C</td>
</tr>
</tbody>
</table>
Two morphologies can be seen in the micrograph (a), one formed by porous monoliths and the other predominantly in the form of agglomerated lobes of different sizes, a homogeneous growth of the particles is not observed, this may be due to the fact that the microwave energy is distributed unevenly, heating from the outside to the inside. In the micrograph (b) details of the lobular growths (1,000 nm) are observed, where it can be seen that the structures have porosity.

The Figure 5 presents the scanning electron micrographs at 5,000X and 50,000X for the TiO$_2$-US sample synthesized by ultrasonic irradiation. The morphology is predominantly constituted by monolithic structures, similar to those found by microwave irradiation, although smaller in size. It can be observed that on the surface of these, there is the formation of incipient lobular particles (a), which fail to agglomerate due to the implosions generated during cavitation, preventing the growth of agglomerates as observed in the sample irradiated by MO (TiO$_2$-MO); generating textural and morphological defects. When zooming in (b) at 50,000X, the lobular structures (500 nm) and fragments of them on the surface, as well as their porosity, are observed in detail.

Therefore, it can be established that the MO irradiation technique promotes the growth and agglomeration of the lobular morphology and the ultrasonic irradiation technique promotes the formation of monoliths.

Figure 6 presents the scanning electron micrographs at 5,000X and 50,000X, for the TiO$_2$-MC sample synthesized by combined mode (microwave-ultrasound).

The micrograph (a) shows the two morphologies found in the samples irradiated by MO and US, predominating the monolithic structure as in the sample synthesized by US (TiO$_2$-US). It is observed
that on the surface of the monoliths there are agglomerated lobular particles and fragments of these, in smaller proportion and size than those found in the sample irradiated only by MO. When magnified at 50,000 X (b) it is observed that the lobular particles are porous (600 nm), and fragments of the lobes caused by cavitation are also observed. In the combined method, the morphology generated is more influenced by ultrasound irradiation than by microwave irradiation.

One can observe agglomerated lobular particles similar to those obtained by microwaves, although smaller in size (a) with a homogeneous distribution. Upon amplification (b) it can be seen that the particles are bound together, they are also porous and similar in size to those found by ultrasound irradiation.

Figure 5. Scanning electron microscopy of TiO$_2$-US a) 5,000 X and b) 50,000 X.

Figure 6. Scanning Electron Microscopy of TiO$_2$-MC a) 5,000 X and b) 50,000 X.

Figure 7. Scanning Electron Microscopy of TiO$_2$-C a) 5,000X and b) 50,000 X.
tion (600 nm). Therefore, the conventional method promotes the morphology integrated by lobular agglomerates.

With the above, it can be established that the thermal treatment during the synthesis with microwaves (TiO$_2$-MO) and reflow (TiO$_2$-C), favors the formation of the lobular morphology; while the treatment with ultrasound, promotes the formation of porous monolithic structures in the TiO$_2$-US and TiO$_2$-MC samples.

One of the objectives of synthesizing this type of materials, by means of synthesis methods that allow modifying morphological and textural properties (microwave, ultrasound and combined mode), is to optimize processes such as photocatalysis by providing a better interaction of light with the catalyst, as a consequence of the modification of these properties. To this end, the band gap energy value for the synthesized materials was also determined to verify if the synthesis techniques modify the optical properties of the synthesized materials.

The values of the band gap energy were obtained by means of the modified KubelkaMunk function.

Where the Kubelka-Munk function is determined by the equation:

\[ F(R) = \frac{(1-R)^3}{2R} \]

(2)

where \( F(R) \) is the function and \( R \) is the reflectance, not considering direct and indirect transitions\[^{28}\]. In order to consider electronic transitions and to have a more accurate edge energy value, the following modified Kubelka Munk function was used:

\[ (F(R) \ast h\nu)^{1/n} \]

(3)

where \( h \) is Planck’s constant (J-s), \( \nu \) is the frequency of light (s) and \( n \) is the coefficient associated with the electron transition, whose value for the indirect transition is equal to 2 and for the direct transition is 1/2.

**Figure 8** shows the graph of the modified Kubelka-Munk function vs \( h\nu \), using the indirect transition. This method is recommended by the López team\[^{29}\], who carried out a study with different graphical methods using both direct and indirect transitions, finding greater precision in the calculation of \( E_g \) using the indirect transition.

The synthesized materials were evaluated in the photodegradation of methyl orange at 5 ppm, with an equilibrium time of 120 min with UV light. In addition, photolysis was performed as a reference.

**Figure 9** shows the photodegradation profile for methyl orange irradiated with UV light.

It is worth mentioning that what makes each synthesized TiO$_2$ sample different is the thermal treatment in the crystallization stage, which generates materials with different morphological, textural and optical properties. The best result observed for photodegradation was for the TiO$_2$-MC sample synthesized by combined microwave-ultrasound mode with a total photodegradation for methyl orange of 100%, followed by TiO$_2$-C synthesized by conventional reflux method with 89% photodegradation. In this case both samples have the same edge energy transitions.
value and what makes the difference towards higher photodegradation is that the TiO$_2$-MC sample has a higher percentage of anatase phase, in smaller crystals (higher availability of active sites) and larger pore area-size, compared to the TiO$_2$-C sample. With the advantage that the synthesis of the photocatalyst is carried out in only 5 min compared to 120 min of the conventional reflux method.

Thus, it can be established that the synthesis methods determine the morphological (crystallinity, crystal size, percentages of phases present, particle shape and size), textural (surface area, pore size and volume) and optical (edge energy) characteristics of the materials studied. Therefore, with microwave-assisted synthesis techniques, ultrasound and the combined microwave-ultrasound method, materials can be designed according to the application, in addition to the reduction of reaction times from hours to minutes.

4. Conclusions

It was possible to synthesize titanium dioxide nanoparticles by ultrasonic microwave and combined mode (reflux) methods, free of crystalline impurities, in 5 min of reaction.

The crystal size, percentages of the phases present (anatase, rutile and brookite), surface area, size and pore volume of the synthesized TiO$_2$ are a function of the synthesis method without affecting the lattice parameters.

The MO irradiation technique promotes the growth and agglomeration of lobular morphology and the ultrasonic irradiation technique promotes the formation of porous monoliths. For the combined method (microwave-ultrasound) the generated morphology is more influenced by ultrasound irradiation.

For the photodegradation of methyl orange, the most efficient photocatalyst was TiO$_2$ synthesized by combined mode (microwave-ultrasound) achieving 100% photodegradation.

The amount of photodegraded contaminant is a function of the textural properties and the percentage of anatase phase in the catalyst at the same Eg value.

Conflict of interest

Authors declared no conflict of interest.

Acknowledgments

The authors thank the National Polytechnic Institute, project SIP: 20171410 and the National Council of Science and Technology for financial support; the IPN Center for Nano and Micro and Nanotechnology for technical support.

References

9. Verbruggen SW. TiO$_2$ photocatalysis for the degradation of pollutants in gas phase: From


26. Nawi MA, Zain S. Enhancing the surface properties of the immobilized degussa P-25 TiO$_2$ for the efficient photocatalytic removal of methylene blue from aqueous solution. Applied Sur-
face Science 2012; 258: 6148–6157.
28. Christy AA, Kvalheim OM, Velapoldi RA.
Quantitative analysis in diffuse reflectance spectrometry: A modified Kubelka-Munk equa-
29. López R, Gómez R. Band-gap energy estimation from diffuse reflectance measurements on