Synthesis of Mesoporous TiO$_2$ Spheres via the Solvothermal Process and Its Application in the Development of DSSC

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This study examined the synthesis of the n-type nanostructured titanium dioxide semiconductor using a combined sol-gel/solvothermal method at 200°C, varying the concentrations of H$_2$O and HCl used as a catalyst for the hydrolysis of the titanium isopropoxide precursor. A white powder of TiO$_2$ nanoparticles was obtained via the solvothermal process. Scanning electron microscopy revealed a spherical morphology of the TiO$_2$ nanoparticles, with their diameter ranging from 2 to 7 microns as the HCl concentration increases. High-resolution electron microscopy and X-ray diffraction showed that the spheres are mesoporous titanium oxide (TiO$_2$m) composed of nanocrystals with an anatase crystalline phase whose crystallite diameter grows from 8 to 13 nm as the HCl concentration increases. On the contrary, optimizing the H$_2$O concentration enabled a decrease in the crystallite size of TiO$_2$m and increases in the surface area and the energy bandgap of TiO$_2$m. The enlarged surface area enabled an increase in the number of contact points between TiO$_2$m and the dye of dye-sensitized solar cells (DSSCs), resulting in a better solar cell performance. The white powder was used to prepare a TiO$_2$m film via the screen-printing technique, which was used in the development of DSSC. The performance parameters of the DSSC (I$_{SC}$, V$_{OC}$, FF, and η%) were correlated with the synthesis parameters of TiO$_2$m. This correlation showed that H$_2$O and HCl greatly influence the semiconductor properties of TiO$_2$m, along with the short-circuit current I$_{SC}$ and the conversion efficiency η% of the DSSC.

1. Introduction

Dye-sensitized solar cells (DSSCs) were developed at the beginning of the 90s [1], and today, they represent a mature technology with high marketing potential due to their acceptable stability, high performance under different lighting conditions, relatively low cost of production, and low toxicity [2–4]. The principle of operation of these cells is based on the separation of electrical charge by the junction between semiconductor materials with different electrical conductivities [5]. The active electrode of a DSSC uses an n-type mesoporous oxide semiconductor with a large surface area as its main component—in most cases, titanium oxide (TiO$_2$)—whose crystalline anatase phase is most often used [6–11].

A DSSC has a structure of the type SnO$_2$:F/TiO$_2$c/TiO$_2$m/N719/I$^-$/I$_3^-$/Pt/SnO$_2$:F, where SnO$_2$:F represents a transparent conductor of high electrical conductivity and optical transmittance, TiO$_2$c is a thin layer of TiO$_2$ called the compact layer, TiO$_2$m is a mesoporous n-type semiconductor layer, N719 is a ruthenium dye, I$^-$/I$_3^-$ is the redox pair, and Pt/SnO$_2$:F represents a platinum counter electrode deposited on the transparent conductor SnO$_2$:F.
During the preparation of the DSSC, the TiO$_2^{m}$ layer is sensitized with a dye (e.g., N719, N3, or organic dyes) to absorb electromagnetic radiation from the sun.

During the electromagnetic excitation from the HOMO (highest occupied molecular orbital) level to the LUMO (lowest unoccupied molecular orbital) level of the N719 dye, an electron is created at the LUMO level and a hole is formed at the HOMO level. From the LUMO level, the electron is rapidly injected into the conduction band of TiO$_2^{m}$ and transferred to SnO$_2$:F through TiO$_2^{m}$ for subsequent extraction to an external circuit connected to the DSSC [3, 12–15]. To regenerate the ionized HOMO level, it is necessary to transfer an electron to that state from the redox pair (for example, I$^-$/I$_3^-$ or Co$^{2+}$/Co$^{3+}$), which donates electrons to restore the original state of the dye [3]. To regenerate the redox pair I$^-$/I$_3^-$, the Pt/SnO$_2$:F counter electrode consisting of a thin layer of platinum functioning as a catalyst is used to facilitate electron collection [16]. Once the photosensitizing of a thin layer of platinum functioning as a catalyst is performed via a sol-gel/solvothermal process, in which the chemical reaction occurring during TiO$_2^{m}$ synthesis [20]. The crystalline anatase phase of TiO$_2^{m}$ is one of the most often used phases in preparing DSSC because it allows high conversion efficiencies to be obtained [21–23].

The solvothermal method has widely been used in the synthesis of the nanoparticles of semiconductor materials [24–28]. If water is used as a solvent, the method is known as “hydrothermal synthesis,” whereas if some alcohol is used, the process is known as “solvothermal synthesis.” Both processes are used to prepare various semiconductor materials of different geometries, such as micro- and nanstructured powders. In addition, it is possible to control the morphology (sphere (3D), rod (2D), or wire (1D)) of the crystals formed via solvent supersaturation, the chemical concentration of the reagents used, and kinetic control [29].

TiO$_2^{m}$ has a relatively large surface area, allowing greater dye and photon adsorption. Among the different mesoporous nanostructured materials, the synthesis of TiO$_2^{m}$ spheres—TiO$_2^{m}$ nanocrystals brought together into spherical assemblies—having a larger surface area than some nanotube and nanowire systems has been demonstrated [30].

Several methods for preparing TiO$_2^{m}$ spheres using different variations of the solvothermal method have been published in the literature. A characteristic of these synthesis methods is that mesoporous spheres are formed in two steps: (a) formation of TiO$_2^{m}$ spheres during a sol-gel process and (b) subjection of these spheres to a solvothermal process in an autoclave at temperatures between 150 and 200°C [31–35]. For example, some authors synthesized TiO$_2^{m}$ precursor spheres from a sol-gel solution in the presence of hexadecylamine, then dried them in the air, and finally subjected them to solvothermal treatment in a mixture of water and ethanol [31, 32]. Another method used to form titania (anatase-rutile) spheres is to add titanium tetraisopropoxide to ethylene glycol to form a white suspension, drying it at 80°C for 10 h. The spheres obtained using this method are dispersed in water and ethanol, placed in an autoclave, and thermally treated at 150°C for 12 h [33]. Another synthesis method of TiO$_2^{m}$ microspheres is the thermal hydrolysis of titanium sulfate, dissolving it later in n-propanol and water, and then performing the solvothermal reaction [34]. The synthesis of TiO$_2^{m}$ microspheres starting from titanium isopropoxide mixed with anhydrous acetone at ambient conditions is also possible by subjecting the mixture to a solvothermal process at 200°C for 12 h [35].

In the present study, the synthesis of TiO$_2^{m}$ spheres is performed via a sol-gel/solvothermal process, in which the structural, morphological, optical, and electrical properties of the spheres are essentially studied according to the concentration of hydrochloric acid (as a catalyst for the hydrolysis of the titanium isopropoxide precursor), the H$_2$O content, and the temperature during the synthesis. Specifically, the surface area of TiO$_2^{m}$, pore size distribution, crystallite size, and forbidden energy band gap $E_g$ are studied. This study also examines the application of TiO$_2^{m}$ in the development of DSSC and the performance parameters (short-circuit current $I_{SC}$, open-circuit voltage $V_{OC}$, fill factor $FF$, and conversion efficiency $\eta$%) as a function of the synthesis parameters of the n-type TiO$_2^{m}$ semiconductor.

2. Experimental Section

2.1. Chemical Reagents. To prepare the different component layers of the DSSC, the following reagents and materials were used.

Titanium isopropoxide (Sigma-Aldrich), ethyl alcohol absolute (Fermont), acetone absolute (Fermont), hydrochloric acid (J. T Baker 36.6–38%), and deionized water (Milli®85-Q/RIO) were used. SnO$_2$:F (FTO) of 15 and 8 ohm per square (TEC15 Pilkington group), terpineol (mixture of isomers anhydrous, Sigma-Aldrich), ethyl cellulose (Sigma-Aldrich), ruthenium dye N719 (Ruthenizer 535-bis TBA Solaronix), polymer Surliny® (Meltonix 1170-60 Solaronix), and Platinum Paste-PT-1 (Dyesol) electrolyte (Lodolyte HI-30) were also used.

2.2. Deposition of DSSC Films and Cell Assembly

2.2.1. TiO$_2^{c}$ Layer. To prepare the thin film called the TiO$_2^{c}$ blocking layer, a mixture of 2.0 mL of deionized water (H$_2$O) with 93.5 mL of ethanol was stirred in a two-neck flat-bottomed flask, adding 1.5 mL of hydrochloric acid (HCl) as a catalyst for the hydrolysis of the titanium isopropoxide precursor $\text{Ti(OCH}_4\text{)}_4$ (TiOC$_4$H$_8$)$_4$ [36–38]. After 20 minutes of stirring, 3 mL of titanium isopropoxide was
added dropwise to the above solution, which was then stirred for 24 h. During the said addition, the titanium precursor is hydrolyzed, forming a sol, to later form the polymer chains of the fully hydrolyzed Ti(OH)₄ monomer and thereby form the gel [39]. Using dip coating equipment, 3 depositions are performed on a transparent conductive glass substrate of SnO₂:F (FTO) with resistivity of 15 Ω/□. Subsequently, the substrate is calcined in air at 450°C, where the metal hydroxide is transformed into a titanium oxide film with a thickness of approximately 200 nm. In this way, a SnO₂:F/TiO₂半导体 junction is obtained.

2.2.2. Synthesis of TiO₂m Nanoparticles via a Sol-Gel/Solvothermal Method

(1) Sol-Gel Process. To prepare TiO₂m nanoparticles, a mixture of 1.9 mL of deionized water (H₂O) with 115.5 mL of ethanol was stirred in a two-neck flat-bottomed flask, adding hydrochloric acid (HCl) as a catalyst for the hydrolysis [36–38]. The volume of HCl was adjusted to obtain 0.5, 1, 1.5, 2, 2.5, and 3% (v/v) concentrations in relation to the total solution volume. After 20 minutes of stirring, 20.73 mL of titanium isopropoxide was added dropwise to the above solution, which was then stirred for 24 h.

(2) Solvothermal Process. After the sol-gel process, the solution was placed in an autoclave and thermally treated for 12 h at 200°C and a pressure of 54 atm. Then, the autoclave was placed in an ultrasound bath for 1 h to avoid nanoparticle agglomeration and lump formation. In another container, 0.15 grams of ethyl cellulose was added to create pores in the TiO₂m layer during the thermal treatment.

2.2.3. Preparation of the TiO₂m Layer. Using the TiO₂m nanoparticles obtained via the solvothermal method explained in the previous section, a paste was prepared with 0.5 g of TiO₂m mixed with 4.0 g of terpineol as a dispersing agent and 2 mL of acetone; this paste was placed in an ultrasound bath for 1 h to avoid nanoparticle agglomeration and lump formation. In another container, 0.15 grams of ethyl cellulose were weighed and mixed with 8 mL of ethanol, and the mixture was also placed in an ultrasound bath for 1 h. Subsequently, both solutions were mixed, and the ethanol was extracted using a rotary evaporator. The remaining paste was deposited using the screen-printing technique on the SnO₂:F/TiO₂m heterojunction with an area of 0.5 × 1.0 cm², which was thermally treated at 530°C for 1 h. Ethyl cellulose was added to create pores in the TiO₂m layer during the thermal treatment.

2.2.4. N-719 Dye. Sensitization of TiO₂m at the SnO₂:F/TiO₂m heterojunction was performed by immersion for 24 h in a 0.5 mM solution of N-719 ruthenium dye in ethanol, which is based on ruthenium-bipyridyl complexes. The N-719 ruthenium dye from Solaronix has the following molecular structure: C₃₈H₆₈O₈N₈S₂Ru. To sensitize the n-type TiO₂m semiconductor, the dye needs to have the capacity to adhere strongly to the surface of TiO₂m, which is achieved through the carboxylic groups of the N-719 dye. The sensitized SnO₂:F/TiO₂m/dye heterojunction is known as the working electrode because a DSSC constitutes a photoelectrochemical cell.

2.2.5. I⁻/I₃⁻ Redox Pair. An electrolyte in a liquid state is a fluid containing ions carrying electric charges. The I⁻/I₃⁻ redox pair was used in this project and is commonly used for these types of cells [40]. To prepare the electrolyte, solutions of lithium salts (lithium iodide), iodine, and 4-tert-butylpyridine dissolved in acetonitrile are usually mixed. The electrolytic solution (lodolyte HI-30 from Solaronix) is placed in the solar cell to regenerate the dye after it has provided an electron to the TiO₂m conduction band; thus, the electrolyte is the medium allowing the oxidized dye to regenerate and, under electromagnetic excitation, continue injecting electrons into the semiconductor.

2.2.6. Counter Electrode. A platinum film is deposited on SnO₂:F to generate the Pt/SnO₂:F counter electrode of the solar cell, considering that Pt is used to expedite electrolyte regeneration. Using the screen-printing technique, a platinum paste (Platinum Paste-PT-1 from Dyesol) was applied on SnO₂:F, allowed to dry for 30 min at room temperature and then thermally treated at 450°C for 1 h.

2.2.7. DSSC Assembly. To assemble the solar cells studied here, the working electrode was placed with the dye facing up; a spacer (Surlyn® Polymer) was placed with a tweezer to avoid electrical contact between the TiO₂m layer and the counter electrode. Previously, Surlyn® was cut in the form of a frame to cover the area around the TiO₂m layer (1.2 cm × 0.7 cm). Then, the counter electrode was placed on the working electrode so that Surlyn was sandwiched between the glasses as shown in Figure 1.

This arrangement was introduced into a muffle furnace at 215°C for 90 s, then removed from the furnace, and allowed to cool at room temperature for 5 min. Subsequently, the electrolytic solution was injected into the cell through a pair of holes previously drilled in the counter electrode. Finally, silver paint was placed on the ends of the cell for better conductivity in measuring its parameters.

2.3. Experimental Equipment. To study the crystalline phase and crystallite size of the n-type TiO₂m semiconductor prepared in this study, we used a Rigaku X-ray diffractometer DMAX-2200, which uses the Kα line (λ = 1.5405 Å) of a copper anode. The crystallite size of TiO₂m was determined using the Scherrer equation:

\[ D = \frac{0.94\lambda}{B \cos \theta} \tag{1} \]

where λ is the X-ray wavelength, B (2θ) is the full-width at half-maximum intensity (FWHM), and θ is the diffraction
To study the surface morphology of TiO$_2$ m, micrographs were obtained by field emission scanning electron microscopy (FE-SEM Hitachi S-5500). Reflectance and optical transmittance analyses were performed with a SHIMADZU UV-3101 spectrophotometer. These analyses were then used to calculate the size of the forbidden energy band gap $E_g$ [41]. For the measurement of the I-V curves, a Keithley 236 Source-Measure Unit coupled with the SLB-150A Compact Solar Simulator Class AAA from SCIENCETECH and equipped with a UXL-150S0 Xenon short-arc lamp and an AM Air Mass Filter, was used. The specific surface area (SSA) was calculated using the BET method on a Quantachrome Autosorb 1. Before nitrogen adsorption, the oven-dried and dispersed sample was placed on a Quantachrome 9 mm cell and outgassed at 100°C for 24 h to remove any adsorbed water after storage and transport of the sample. Nitrogen adsorption isotherms were programmed with a 44 data point collection, of which the first 11 were used for SSA calculations.

3. Results and Discussion

3.1. Influence of HCl as a Catalyst for Hydrolysis on the Synthesis of TiO$_2$ m Nanoparticles. During the synthesis of TiO$_2$ m nanoparticles via the solvothermal method, the volume of HCl (experimental parameter) as a catalyst for hydrolysis was varied in relation to the total solution volume (% (v/v)) according to the following values: 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0% (v/v). The H$_2$O concentration was fixed during this process at 1.9% (v/v). The TiO$_2$ m nanoparticles prepared using this method were characterized by X-ray diffraction and FE-SEM. This experiment showed that HCl, as a catalyst for the hydrolysis of titanium isopropoxide, plays a fundamental role in the properties of TiO$_2$ m nanoparticles synthesized during the sol-gel/solvothermal process as described below.

3.1.1. TiO$_2$ m Nanoparticles Prepared via the Solvothermal Process at 200°C. Figure 2 shows the X-ray diffraction patterns of TiO$_2$ m nanoparticles prepared at 200°C in an autoclave as a function of HCl concentration. Other reflections corresponding to its other crystalline planes are observed. Relatively wide peaks corresponding to relatively small crystallite sizes (8–12 nm), as discussed below, are observed.

3.1.2. Thermal Treatment of TiO$_2$ m Nanoparticles in Air at 530°C. As explained in Section 2.2.3, a paste was made with TiO$_2$ m nanoparticles prepared using the solvothermal process for the deposition of the mesoporous layer via the screen-printing technique on the SnO$_2$:F/TiO$_2$ c junction to obtain the SnO$_2$:F/TiO$_2$ c/TiO$_2$ m heterojunction, which was thermally treated in air at 530°C for 3 h. After thermal treatment, an X-ray diffraction study was performed on each sample listed in Figure 2, with the results shown in the graph of Figure 3. This graph shows that the anatase crystalline phase is conserved for all HCl concentrations, except for 2.5 and 3.0% (v/v) HCl concentrations, where a small peak can be perceived ($R$) at an angle of $2\theta = 27.2^\circ$, corresponding to the rutile crystalline phase. With thermal treatment, diffraction peaks are sharper, so the crystallite size has increased (17 to 22 nm), as reported in Table 1.

3.1.3. FE-SEM of TiO$_2$ m Prepared at Different HCl Concentrations. Figure 4 shows micrographs of the surface morphology of TiO$_2$ m taken with the FE-SEM S-5500 microscope (10,000X) for each HCl concentration used during the sol-gel/solvothermal process at 200°C. These micrographs show how the HCl concentration significantly influences the morphology of TiO$_2$ m particles, which changes from a relatively smooth surface, as observed in Figures 4(a) and 4(b), corresponding to the synthesis of TiO$_2$ m at 0.5 and 1.0% (v/v) HCl concentrations, respectively, to one in which agglomeration of TiO$_2$ m particles begins, as shown in Figure 4(c), corresponding to a 1.5% (v/v) HCl concentration.
shows a semispherical morphology corresponding to the 2.0% (v/v) HCl concentration, where a clear coalescence is observed as larger spheres grow from the fusion with smaller spheres of TiO$_2$ m. As the HCl concentration increases to 2.5 and 3.0% (v/v), more perfect and larger TiO$_2$ m spheres with diameters above 6 microns are obtained (Figure 4(e)), and Figure 4(f) shows even larger TiO$_2$ m spheres with irregular agglomerates beginning to grow on their surfaces. Notably, Kim et al. [42] also reported the synthesis of TiO$_2$ m spheres in acid media (a mixture of H$_2$SO$_4$ and HNO$_3$) using surfactants as nucleation precursors during the sol-gel process and a subsequent hydrothermal treatment to obtain highly spherical morphologies such as those shown in this study.

Figures 5 and 6 show images of the TiO$_2$ m samples included in Figure 4 at a 300,000X and 500,000X magnification, respectively, where each sample, including the spheres, are made of TiO$_2$ m nanocrystals. Figures 5 and 6 show that all samples have pores and that the pore diameter grows from 10 to 23 nm when the HCl concentration increases from 0.5 to 3.0% (v/v).

The magnification increase from 300,000X to 500,000X allowed us to observe in a much better form the surface morphology as well as the pore size distribution of TiO$_2$ m synthesized at different HCl concentrations. For example, from Figures 4(a)–4(d), it is easy to see a pore size increase as the HCl concentration varies from 0.5 to 2.0% (v/v), and after that, the pore size remains almost constant. Also, the crystal size can be much better estimated, as shown in Figure 6, and its value coincides with the determined by X-ray diffraction (8–12 nm), as explained in Section 3.1.1.

### 3.1.4. Surface Area, Crystallite Size, Pore Size, and $E_g$ of TiO$_2$ m as a Function of HCl Concentration.

Table 1 shows the average crystallite diameter, pore size, surface area, and band gap $E_g$ of TiO$_2$ m samples prepared in an autoclave at 200°C and at 530°C.

<table>
<thead>
<tr>
<th>HCl% (v/v)</th>
<th>Crystallite size (nm) 200°C</th>
<th>Pore size (nm) 200°C</th>
<th>Surface area (m$^2$/g) 200°C</th>
<th>Crystallite size (nm) 530°C</th>
<th>Pore size (nm) 530°C</th>
<th>Surface area (m$^2$/g) 530°C</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.45</td>
<td>2.96</td>
<td>161.10</td>
<td>22.20</td>
<td>10.72</td>
<td>31.75</td>
<td>3.18</td>
</tr>
<tr>
<td>1.0</td>
<td>9.93</td>
<td>4.21</td>
<td>196.00</td>
<td>19.90</td>
<td>12.35</td>
<td>47.30</td>
<td>3.23</td>
</tr>
<tr>
<td>1.5</td>
<td>11.54</td>
<td>15.12</td>
<td>183.90</td>
<td>17.60</td>
<td>41.11</td>
<td>65.56</td>
<td>3.27</td>
</tr>
<tr>
<td>2.0</td>
<td>11.50</td>
<td>6.57</td>
<td>208.70</td>
<td>20.00</td>
<td>23.56</td>
<td>55.46</td>
<td>3.31</td>
</tr>
<tr>
<td>2.5</td>
<td>11.75</td>
<td>5.96</td>
<td>208.10</td>
<td>19.30</td>
<td>19.75</td>
<td>56.83</td>
<td>3.25</td>
</tr>
<tr>
<td>3.0</td>
<td>12.05</td>
<td>6.43</td>
<td>198.50</td>
<td>18.40</td>
<td>16.83</td>
<td>60.12</td>
<td>3.32</td>
</tr>
</tbody>
</table>

Table 1: Crystallite diameter, pore size, surface area, and band gap $E_g$ of TiO$_2$ m samples prepared in an autoclave at 200°C and at 530°C.
Considering the results of Table 1, columns 4 and 7 show the surface area of TiO$_2^{m}$ as a function of HCl concentration for samples treated at 200°C (solvothermal process) and at 530°C, respectively. The surface area decreases drastically from an average of 198 to 52 m$^2$/g as the temperature changes from 200 to 500°C. This decrease in surface area is due to crystallite size growth (diameter), as observed from columns 2 and 5, and to particle coalescence into spherical configurations to form larger TiO$_2^{m}$ spheres, favoring the increase in pore size observed in columns 2 and 6 of Table 2.

Columns 3 and 6 show a maximum pore size of 15.12 nm at 200°C and 41.11 nm at 530°C, both at 1.5% (v/v) HCl concentration. The pore size decreases above the 1.5% (v/v) HCl concentration. This decrease can be attributed to a competition between the decrease in crystallite size from 20.0 to 18.4 nm shown in Table 1 and the formation of larger TiO$_2^{m}$ spheres as the HCl concentration increases above 1.5% (v/v).

Figure 4: Micrographs of TiO$_2^{m}$ (10,000X magnification) synthesized at different HCl concentrations: (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5%, and (f) 3.0% (v/v).
3.2. Influence of H2O during Hydrolysis on the Synthesis of TiO2m Nanoparticles

3.2.1. TiO2m Samples Obtained at Different H2O Concentrations. Once the effect of HCl concentration on preparing TiO2m via the solvothermal process was studied, the role of the H2O content during the synthesis of TiO2m was analyzed. To this end, X-ray diffraction studies were performed on the TiO2m films prepared via the solvothermal process at 200°C, taking the 2.5% (v/v) HCl concentration as a fixed experimental parameter and varying the H2O concentration from 1.9 to 4.9% (v/v). All cases show an X-ray diffraction pattern of the TiO2m anatase crystalline phase very similar to that in Figure 2. It was also observed that for the 3.9% (v/v) H2O concentration, there are small indications of the growth of a brookite phase at an angle of $2\theta = 30.8^\circ$ corresponding to the (121) plane.

3.2.2. TiO2m Samples Treated at 530°C. Because the TiO2m layer in the development of DSSC was thermally treated in air at 530°C for 3 h, after calcining at that temperature, these samples were subjected to an X-ray diffraction study.
The diffraction pattern found in these samples is very similar to that shown in Figure 3 for samples prepared at different HCl concentrations. Here, the anatase crystalline phase is conserved for all H₂O concentrations except for 2.5 and 3.0% (v/v), where a small peak can be perceived at \(2\theta = 27.5^\circ\), corresponding to the rutile crystalline phase (R). On the contrary, it is also possible to observe that after said thermal treatment at 530°C, the brookite phase disappears for all H₂O concentrations at which it could be observed.
3.2.3. Analysis of the TiO$_2^{m}$ Surface Area and Pore Size as a Function of H$_2$O Concentration. For use in the development of DSSC, TiO$_2^{m}$ powders should be thermally treated at 530°C in air for 3 h. Table 2 shows the average crystallite diameter, surface area, and pore size of TiO$_2^{m}$ samples prepared at different H$_2$O concentrations, maintaining the HCl concentration at 2.6% (v/v) and thermally treated in air at 530°C.

Comparing the columns pertaining to crystallite size in Tables 1 and 2, one finds that for treatment at 530°C, on average (not shown in tables), the TiO$_2^{m}$ crystallite size decreases more with increasing H$_2$O content (17.3 nm) than with increasing HCl concentration (19.56 nm), and consequently, the surface area and forbidden band of TiO$_2^{m}$ should grow slightly with increasing H$_2$O concentration. Similarly, by comparing the corresponding columns for the pore size shown in Tables 1 and 2, one finds that for treatment at 530°C, on average, a larger TiO$_2^{m}$ pore size is more favored by increasing the concentration of H$_2$O (24.34 nm) than by increasing that of HCl (20.72 nm).

The findings described in the previous paragraph should be revealed by an increase in the surface area upon optimizing the H$_2$O concentration. Indeed, by comparing the columns pertaining to the surface area in Tables 1 and 2, one finds that for treatment at 530°C, on average, a larger TiO$_2^{m}$ surface area is more favored by an increase in H$_2$O concentration (63.97 m$^2$/g) than by an increase in HCl concentration (52.83 m$^2$/g). An increasing surface area increases the number of contact points between TiO$_2^{m}$ and the dye, and this is reflected in the solar cell performance as seen later.

3.3. TiO$_2^{m}$ Crystallite Size as a Function of HCl and H$_2$O Concentrations. Curve (a) in Figure 7 shows the crystallite size of TiO$_2^{m}$ in samples prepared in the autoclave at a temperature of 200°C as a function of HCl concentration, maintaining a fixed 1.9% (v/v) H$_2$O concentration. As shown in Table 1, the crystallite size increases from 8.45 to 11.04 nm as the HCl concentration increases from 0.5 to 1.5% (v/v); above this last value, the crystallite grows more slowly and reaches a constant value close to 12 nm. This behavior could be due to the hydrolysis of titanium isopropoxide, in which the substitution of the isopropoxy groups O(C$_3$H$_7$) of titanium isopropoxide by OH$^-$ groups is relatively slow, and as HCl is added, hydrolysis speeds up, causing an increase in crystallite size up to a concentration of 1.5% (v/v), at which the chemical bonds between Ti$^{IV}$ and OH$^-$ hydroxyl radicals reach saturation. Above the 1.5% (v/v) HCl concentration, the crystallite growth is very slow and almost constant. Curve (b) in Figure 7 shows the crystallite sizes of TiO$_2^{m}$ prepared in the autoclave at 200°C by varying the H$_2$O concentration and taking as a fixed parameter a 2.5% (v/v) HCl concentration. From that curve, it is possible to observe that the crystallite size of the TiO$_2^{m}$ semiconductor undergoes a slight decay from 11.8 to 10.6 nm as the H$_2$O concentration increases from 1.9 to 4.9% (v/v).

3.4. Forbidden Energy Band Gap of TiO$_2^{m}$ as a Function of HCl and H$_2$O Concentrations. According to the theory of quantum confinement, when the size (diameter) of a crystallite in a crystalline solid decreases to a few nanometers (2–20 nm), the magnitude of the forbidden energy band gap varies. To calculate the forbidden energy band gap $E_g$ of TiO$_2^{m}$ nanoparticles were synthesized at different HCl and H$_2$O concentrations and thermally treated in air at 530°C. Because TiO$_2^{m}$ has an indirect energy band, a graph of $(\alpha \cdot h\nu)^{1/2}$ vs. $h\nu$ was drawn. In this mathematical expression, $\alpha$ is the absorption coefficient of TiO$_2^{m}$ and is calculated using equation (2), where $d$ is the film thickness, $T$ is the transmittance, and $R$ is the optical reflectance of the material [44].

The tangent line to the curve intersecting the $h\nu$ axis indicates a very approximate value of the forbidden energy band gap:

$$\alpha = \frac{1}{d} \ln \left( \frac{100 - R}{T} \right).$$

Following the procedure described above, the value of the indirect energy band gap $E_g$ was determined for each HCl concentration used during the synthesis of TiO$_2^{m}$, maintaining a 1.9% (v/v) H$_2$O concentration as a fixed parameter. Curve (a) in Figure 8 shows the values of the indirect energy band gap $E_g$ determined for each HCl concentration used for the synthesis of TiO$_2^{m}$. As the HCl concentration increases from 0.5 to 2% (v/v) in the synthesis of the particles, $E_g$ decreases from 3.375 to 3.18 eV; above this concentration, $E_g$ increases slightly until reaching 3.26 eV. These results suggest that optical properties, particularly the absorption coefficient of TiO$_2^{m}$, depend on the synthesis of the material [45].

Curve (b) in Figure 8 shows the magnitude of the indirect forbidden energy band gap $E_g$ of TiO$_2^{m}$ treated at 530°C (HCl concentration = 2.5% (v/v)). This figure shows that the forbidden energy band gap increases from 3.18 to 3.32 eV when the H$_2$O content varies from 1.9 to 4.9% (v/v). The growth in the magnitude of the forbidden energy band gap is consistent with the decrease in crystallite size from 19.3 to 17.1 nm shown in Table 2, which can be attributed to a quantum confinement effect, as explained by Sánchez et al. [46].

**Table 2: Crystallite diameter, surface area, pore size, and forbidden energy band gap $E_g$ of TiO$_2^{m}$ samples thermally treated in air at 530°C as a function of the H$_2$O concentration.**

<table>
<thead>
<tr>
<th>H$_2$O% (v/v) (530°C)</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore size (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>19.30</td>
<td>56.83</td>
<td>19.75</td>
<td>3.18</td>
</tr>
<tr>
<td>2.4</td>
<td>18.40</td>
<td>56.29</td>
<td>17.19</td>
<td>3.23</td>
</tr>
<tr>
<td>2.9</td>
<td>18.10</td>
<td>62.52</td>
<td>33.14</td>
<td>3.27</td>
</tr>
<tr>
<td>3.4</td>
<td>16.60</td>
<td>68.15</td>
<td>30.89</td>
<td>3.31</td>
</tr>
<tr>
<td>3.9</td>
<td>16.90</td>
<td>71.40</td>
<td>22.93</td>
<td>3.25</td>
</tr>
<tr>
<td>4.9</td>
<td>17.10</td>
<td>66.84</td>
<td>22.17</td>
<td>3.32</td>
</tr>
</tbody>
</table>
3.5. Photovoltaic Performance Analysis of DSSC

3.5.1. Effect of HCl on the Photovoltaic Performance of DSSC.

Once the TiO$_2$ m semiconductor was prepared, the DSSC was assembled with a structure of the type SnO$_2$: F/TiO$_2$ c/TiO$_2$ m/N719/I$_{-}$/I$_3$ -/I$^-$/Pt/SnO$_2$: F. Here, the TiO$_2$ m layers were thermally treated in air at 530°C, having a thickness close to 12 microns.

Figure 9 shows the current-voltage curves (I-V) for the different HCl concentrations used in the synthesis of the n-type TiO$_2$ m semiconductor via the solvothermal process. As shown, the HCl concentration drastically influences the performance of the DSSC, where the parameter most influenced is the short-circuit current density $J_{SC}$ and thus the conversion efficiency $\eta$% of the solar cell.

The short-circuit current density $J_{SC}$ starts at 4.2 mA/cm$^2$ for the 0.5% (v/v) HCl concentration and reaches a value of 10.14 mA/cm$^2$ for the 2.0% (v/v) HCl concentration; above this concentration, $J_{SC}$ decreases to 8.83 mA/cm$^2$ for the 3.0% (v/v) HCl concentration.

Table 3 summarizes the performance parameters of the DSSC shown in Figures 9 and 10, that is, the open-circuit voltage ($V_{OC}$), the short-circuit current density ($J_{SC}$), the fill factor (FF), and the energy conversion efficiency ($\eta$%) of the DSSC obtained by varying the concentration of HCl as a catalyst for the hydrolysis of titanium isopropoxide as well as the H$_2$O content during the sol-gel/solvothermal process.

With the data presented at the left side of Table 3, Figure 10(a) shows a graph of the short-circuit current $J_{SC}$ as a function of the concentration of HCl for the hydrolysis, showing a maximum at $J_{SC}$ = 10.14 mA/cm$^2$ and 2.0% (v/v) HCl.

The conversion efficiency $\eta$% shows a behavior analogous to that of $J_{SC}$. As shown in Figure 10(b), as the concentration of the HCl hydrolysis catalyst is increased from 0.5 to 2.5% (v/v), $\eta$% increases from 2.06% to 3.91%. Above this HCl concentration (2.5% (v/v)), $\eta$% decreases to 3.69%.

Table 3 (left side) shows a small variation in the open-circuit voltage $V_{OC}$ upon increasing the concentration of HCl for the hydrolysis from 0.5 to 2.5% (v/v). In this case, the open-circuit voltage $V_{OC}$ decreases slightly from 0.73 to 0.68 V and then increases again to 0.7 V at the 3.0% (v/v) HCl concentration, yielding an average value of $V_{OC}$ = 0.695. Likewise, the fill factor (FF) decreases from 0.68 to 0.52 as the HCl concentration increases from 0.5 to 2.0% (v/v) and then increases again slightly to 0.59 at the 3.0% (v/v) HCl concentration, for an average value of FF = 0.616.

3.5.2. Effect of the H$_2$O Content on the Photovoltaic Performance of DSSC.

Figure 11 shows the I-V curves of DSSC utilizing the TiO$_2$ m semiconductor prepared with a 2.5% (v/v) HCl concentration for the hydrolysis of titanium isopropoxide and varying H$_2$O content during the sol-gel/solvothermal process. According to Figure 10(b), 2.5% (v/v) HCl concentration optimizes the efficiency of the DSSCs prepared using the TiO$_2$ m semiconductor. Table 3 (right side) shows the performance parameters of the DSSC shown in Figure 11: $V_{OC}$, $J_{SC}$, FF, and $\eta$% of the DSSC obtained by varying the H$_2$O content.

The right side of Table 3 shows that DSSC prepared from TiO$_2$ m synthesized at different H$_2$O contents have more uniform and less disperse values of the open-circuit voltage $V_{OC}$ and fill factor (FF) than the corresponding values found at the left side of Table 3 for TiO$_2$ m synthesized at different
Table 3: Performance parameters of solar cells. Left side: DSSCs utilizing TiO$_2$ nm synthesized via a sol-gel/solvothermal process at different HCl concentrations and at a 1.9% (v/v) H$_2$O concentration and thermally treated in air at 530°C. Right side: DSSCs prepared from TiO$_2$ nm synthesized at different H$_2$O contents and at a 2.5% (v/v) HCl concentration for the hydrolysis and thermally treated in air at 530°C.

<table>
<thead>
<tr>
<th>HCl% (v/v)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA·cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>H$_2$O% (v/v)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA·cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.73</td>
<td>4.20</td>
<td>0.68</td>
<td>2.06</td>
<td>1.9</td>
<td>0.68</td>
<td>9.54</td>
<td>0.60</td>
<td>3.91</td>
</tr>
<tr>
<td>1.0</td>
<td>0.69</td>
<td>6.76</td>
<td>0.68</td>
<td>3.15</td>
<td>2.4</td>
<td>0.68</td>
<td>9.38</td>
<td>0.63</td>
<td>4.07</td>
</tr>
<tr>
<td>1.5</td>
<td>0.68</td>
<td>8.61</td>
<td>0.63</td>
<td>3.65</td>
<td>2.9</td>
<td>0.70</td>
<td>7.27</td>
<td>0.64</td>
<td>3.26</td>
</tr>
<tr>
<td>2.0</td>
<td>0.69</td>
<td>10.14</td>
<td>0.52</td>
<td>3.66</td>
<td>3.4</td>
<td>0.69</td>
<td>8.44</td>
<td>0.64</td>
<td>3.69</td>
</tr>
<tr>
<td>2.5</td>
<td>0.68</td>
<td>9.54</td>
<td>0.60</td>
<td>3.91</td>
<td>3.9</td>
<td>0.68</td>
<td>9.45</td>
<td>0.63</td>
<td>4.08</td>
</tr>
<tr>
<td>3.0</td>
<td>0.70</td>
<td>8.83</td>
<td>0.59</td>
<td>3.69</td>
<td>4.9</td>
<td>0.67</td>
<td>9.16</td>
<td>0.65</td>
<td>3.99</td>
</tr>
</tbody>
</table>

Figure 9: I-V curves of DSSC with n-type semiconductors prepared at different concentrations of HCl as a catalyst for the hydrolysis.

Figure 10: (a) Behavior of the short-circuit current $J_{SC}$ and (b) conversion efficiency as a function of the concentration of HCl for the hydrolysis.
HCl concentrations. The open-circuit voltage $V_{OC}$ remains almost constant around its average value of 0.685 V when there is a variation in H$_2$O content, in contrast to an average value of $V_{OC} = 0.695$ V when there is a variation in HCl concentration. Likewise, the fill factor (FF) remains almost constant around its average value of 0.631 when there is a variation in H$_2$O content, in contrast to an average value of FF = 0.616 when there is a variation in HCl concentration.

By comparing the average values of the short-circuit currents $J_{SC}$ of the DSSCs in Figures 9 and 11, one finds that the average $J_{SC}$ (H$_2$O; $J_{SC} = 8.873$ mA/cm$^2$) of the DSSC in Figure 11 surpasses that in Figure 9 (HCl; $J_{SC} = 8.13$ mA/cm$^2$), so the average conversion efficiency of the solar cells in Figure 11 ($\eta\% = 3.83\%$) exceeds the average conversion efficiency of the corresponding ones in Figure 9 ($\eta\% = 3.35\%$).

3.6. On the Method of Preparing Mesoporous Spheres and the Conversion Efficiency Achieved. There is a substantial difference between the preparation methods for mesoporous spheres described in the introduction and the one developed in this study. In the previous methods [31–35], the mesoporous spheres are formed in the first step of the sol-gel solution, then extracted, dried, and passed to the solvothermal process in an autoclave. In the present method, TiO$_2$ microspheres are formed within the autoclave under the influence of a coalescence process at 200°C and HCl, which, with increasing concentration, produces larger mesoporous spheres, as observed in the FE-SEM studies shown in Figure 4.

For comparison purposes of the results obtained in this work, in the literature, it is possible to find other research works related to the synthesis of TiO$_2$ microspheres with an anatase crystalline phase and its application in dye-sensitized solar cells.

Zhao-Qian and coworkers developed a modified solvothermal process to carry out the synthesis of TiO$_2$ microspheres using acetone as solvent [35]. As-prepared TiO$_2$ spheres with diameters from 550 to 1010 nm are composed of densely interconnected nanocrystals with each other and possess a high specific surface area up to 138.47 m$^2$·g$^{-1}$. As n-type semiconductor integrated in DSSC, Zhao-Qian and coworkers prepared TiO$_2$ microsphere films via screen printing. With the work electrode (dye-sensitized TiO$_2$ microspheres), DSSC provided a power conversion efficiency of 7.80%. Finally, TiO$_2$ microsphere-based DSSCs were optimized by adding a TiO$_2$ nanocrystal underlayer and TiCl$_4$ post-treatment providing a better performance.

In addition, Swathy et al. prepared anatase titania microspheres by a modified sol-gel method [47]. At first, they took a defined amount of titanium (IV) butoxide (TB) and ethylene glycol, which were mixed and stirred constantly for 24 hours. Subsequently, to the previous solution, they added a water-acetone mixture. The final precipitate was washed, filtered, and dried. The powder obtained, which was further heat treated at 500°C, contained spherical titania particles with a diameter of ~400 nm. The titania microspheres were then utilized to make TiO$_2$ paste using ethanol as solvent. The size of TiO$_2$ hollow spheres was about 170–300 nm, and the thickness of the shell was about 55–60 nm. TiO$_2$ hollow spheres were utilized as a scattering layer in dye-sensitized solar cells (DSSCs), Swathy et al. deposited the scattering layer by screen printing on a nanocrystalline titania coating. DSSC with scattering layer achieved photovoltaic parameters, such as $V_{OC}$ of 0.690 V, $J_{SC}$ of 10.44 mA/cm$^2$, fill factor of 0.68, and a conversion efficiency of 4.92%.

Another work on the preparation of anatase TiO$_2$ spheres is that reported by Ch. Dwivedia et al. where TiO$_2$ hollow spheres were synthesized in a continuous spray pyrolysisis reactor, using titanium isopropoxide as organic precursor and ethanol as solvent [48]. TiO$_2$ powder was collected from the outlet of the furnace. This powder was then utilized to make TiO$_2$ paste using ethanol as solvent. The size of TiO$_2$ hollow spheres was about 170–300 nm, and the thickness of the shell was about 55–60 nm. TiO$_2$ hollow spheres were utilized as a scattering layer in dye-sensitized solar cells (DSSCs). Commercial nanocrystalline TiO$_2$ paste (20 nm) forming the transparent layer was from Dyesol. DSSC containing TiO$_2$ hollow spheres layer showed a power conversion efficiency of 7.46% which is better than that containing single layer TiO$_2$ transparent film (7.1%).

Finally, Miao et al. also prepared mesoporous anatase TiO$_2$ microspheres with different surface areas obtained by a solvothermal process [49]. To do so, tetrabutyl titanate (TBT) was slowly added to an acetone-phenol mixed solvent under vigorous stirring at room temperature. The resulting solution was transferred into a 40 mL Teflon-lined stainless steel autoclave, and then heated at 150°C for 24 h. The samples were then sintered at 500°C. By tuning the ratio of the mixed solvent, the authors obtained high-quality TiO$_2$ microspheres with controllable surface areas of 122–168 m$^2$·g$^{-1}$. Then, the mesoporous anatase TiO$_2$ microspheres were used as the
scattering layer of the photoelectrode. DSSC based on a photoelectrode with a TiO₂ nanoparticle underlayer and a microsphere scattering layer yield the highest photoelectrical conversion efficiency of 7.94%.

In summary, we have seen that TiO₂ microspheres can be synthesized by several preparation methods utilizing different titanium precursors and solvents. TiO₂ microspheres synthesized here (Table 1) or reported in the literature have a large surface area, are mesoporous, and can be used for light scattering in DSSC, allowing for a good charge collection efficiency.

On the contrary, to explain the reason for the relatively low conversion efficiency (4.07%) obtained in the DSSC prepared here, it should be understood that the use of mesoporous spheres in the TiO₂ₘ semiconductor layer has certain disadvantages compared to a compact and homogeneous mesoporous layer (nanoparticle underlayer or nanocrystalline titania coating) of TiO₂ₘ: (a) There are gaps between spheres that do not contribute to the formation of the TiO₂ₘ/dye junctions. (b) The spherical morphology reduces the surface area, lessening contact between TiO₂ₘ and the dye. (c) The spherical morphology reduces the number of electronic paths for electric current transport after dye excitation. All these facts are detrimental to the conversion efficiency of the DSSC developed here.

To increase the conversion efficiency of the DSSC developed in this study, it would be very convenient to work with the following alternatives in the near future:

(a) Mix TiO₂ₘ spheres with TiO₂ₚ in powder form (called nanoparticle underlayer or nanocrystalline titania coating) without a spherical morphology to fill the gaps between TiO₂ₘ spheres and thus build DSSC.

(b) Use a mesoporous TiO₂ₚ layer in powder form (without a spherical morphology), depositing the mesoporous spheres on that layer, that is, build the solar cell heterostructure with the configuration SnO₂:F/TiO₂ₖ/TiO₂ₚ/TiO₂ₘ/N719/T/IL/Pt/SnO₂:F. In the said heterostructure, the TiO₂ₘ layer would function as a scattering layer, as already reported in the literature, which would result in a structure with greater conversion efficiency [50].

4. Conclusions

The structure and morphology of the TiO₂ₘ nanoparticles prepared via a sol-gel/solvothermal method are greatly influenced by the HCl and H₂O concentrations used during hydrolysis of the titanium isopropoxide precursor. HCl greatly changes the morphology of TiO₂ₘ and, as a function of concentration, contributes to obtaining either a planar configuration or a spherical morphology, that is, mesoporous microspheres. On the contrary, optimizing the H₂O concentration enabled a decrease in the crystallite size of TiO₂ₘ and consequently increases in the surface area, pore size, and energy band gap of TiO₂ₘ. The increase in surface area allowed the number of contact points between TiO₂ₘ and the dye to increase, which was positively reflected in the solar cell performance. However, in all the synthesis processes performed in this study, it was possible to obtain TiO₂ₘ in a predominantly anatase crystalline phase.

The HCl and H₂O concentrations during the synthesis of the n-type TiO₂ₘ semiconductor also have an important influence on the behavior of the performance parameters of the DSSC (Iₛₜ, Vₒₜₐₜ, FF, and η%). By varying the concentration of the catalyst (HCl) during hydrolysis of the precursor, a greater variation in the short-circuit current Iₛₜ is observed in the I-V curve of the DSSC, with a greater dispersion of the values of the performance parameters of the solar cells (Iₛₜ, Vₒₜₐₜ, FF, and η%).

On the contrary, by optimizing the H₂O concentration during the synthesis of the n-type TiO₂ₘ semiconductor, in the analyzed DSSC, the values of the open-circuit voltage Vₒₜₐₜ and fill factor (FF) are more uniform and less dispersed than those for TiO₂ₘ synthesized at different HCl concentrations. On average, the short-circuit currents Iₛₜ and conversion efficiency η% of the cells whose synthesis of TiO₂ₘ was optimized by adjusting the H₂O content surpass those optimized by adjusting only the HCl concentration. The highest conversion efficiency (η%) found in the DSSC reported in this study was 4.08%.

In summary, the performance parameters (Iₛₜ, Vₒₜₐₜ, FF, and η%) of DSSC were greatly influenced by the HCl and H₂O concentrations used during hydrolysis of the titanium isopropoxide precursor in the synthesis of the n-type TiO₂ₘ semiconductor.

Data Availability

This research article is the result of the Ph.D. dissertation in Engineering and Applied Sciences of the student Sergio Velazquez Martinez carried out in the Research Institute of Basic and Applied Sciences of the Autonomous University of the State of Morelos, Mexico. The data of said results are available in the student’s work log which is available in the aforementioned institute.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References


