FULL PAPER

Synthesis and Evaluation of the Photocatalytic Activity of Nanostructured Composites Based on SiO₂ Recovered by TiO₂

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Abstract:

Almost spherical SiO₂ nanoparticles were recovered by thin films of TiO₂ (highly crystalline anatase) produced in situ sol-gel syntheses. Silica coating was proven by scanning electron microscopy and infrared measurements. The outstanding photocatalytic efficiency of this material was proven by the degradation of the dye Ponceau 4R (P4R) in aqueous solution, by monitoring its discoloration as well as by the photocatalytic production of gaseous hydrogen. In the first case, the color of the solutions submitted to the photocatalytic process was reduced to zero in 140 minutes of reaction. Regarding the hydrogen production, 5.5 mmol of H₂ were obtained in 5 hours of reaction, corresponding to a specific rate of production of 13.6 mmol g⁻¹h⁻¹, a value much higher than that obtained using TiO₂ P25 (2.66 mmol g⁻¹h⁻¹) under similar conditions, or even with other photocatalysts reported in the literature. This outstanding photocatalytic activity is coherent with the specific surface area and porosity (respectively 70 m²/g and 15%), estimated for this material. On the other hand, this material presents noticeably superior band gap energy (E₉), 3.3 eV, when compared to the typical values found for TiO₂. This small discrepancy, of 3%, may be the result of the mixture of electronic states of both materials.

Keywords: titanium dioxide; sol-gel synthesis; TiO₂/SiO₂ composite; heterogeneous photocatalysis; production of H₂

1. Introduction

Titanium dioxide is widely used in environmental photocatalysis [1-3], also showing potential application in the photocatalytic production of hydrogen and in dye solar cells [4-7]. However, the aggregation of TiO₂ nanoparticles tends to reduce their specific surface area altering several intrinsic characteristics of the material that end up compromising its application as photocatalyst [8-10].

Its immobilization on the surface of an inert material can be a good strategy to minimize aggregation and related problems, in addition to facilitating the recovery of the catalyst for subsequent reuse. In recent years, the use of photocatalysts immobilized in different materials has shown to be a good strategy to circumvent these difficulties [11-13].

By owning a well-known surface chemistry, optical transparency, thermal and mechanical stability, low cost, easy preparation, high surface area, and to a certain extent, for being photochemically inert [14-16], SiO₂ fits perfectly as a support material [17]. In this way, the immobilization of TiO₂ on SiO₂ surface can lead to a better thermal stability for TiO₂ [14]. In addition, this should increase the photocatalytic activity due to the less tendency to aggregation, provided by silica [18], as well as the presence of vacancies of oxygen in the TiO₂ supported, which may increase...
the delay of recombination between the photogenerated pairs [19] and a higher ability of adsorption of reagents [20].

In the present work, nanoparticles of SiO$_2$ were used as structural support for the purpose of increase the photocatalytic activity of TiO$_2$. The synthesized material was characterized by different techniques, besides having had its photocatalytic activity evaluated both in terms of degradation of organic matter and production capacity of H$_2$.

2. Results and Discussion

2.1 Characterizations

After synthesis and posterior treatments, the TiO$_2$/SiO$_2$ composite was characterized by x-ray diffraction in order to check your structure and crystalline phase (Figure 1). Based on the JCPDS (21-1272) crystallographic record it was verified the existence of only a highly crystalline anatase phase. It is very probable that this is due to the heat treatment performed in combination with the presence of silica, which guarantees a higher thermal stability to the anatase phase [14].

The peaks related to anatase correspond to the values of 2$\theta$ equal to 25.4º, 37.8°, 38.4°, 48.0°, 54.1°, 55.2°, 62.5°, 69.0°, 70.2°, 75.3° and 82.7°, identified in the diffratogram, Figure 1, which correspond respectively to the planes (101), (004), (112), (200), (105), (211), (204), (116), (220), (215) and (224). The peaks identified at 44.5°, 64.9° e 78.3° are related to the constituent material of the sample holder (aluminum), according to JCPDS crystallographic record (1-1180). The absence of peaks referring to silica is due the fact that this material is present in amorphous form (Figure S1) [21].

By applying the Scherrer equation [22], the average size of the crystallites was estimated as being equal to 10 nm. From what has been reported in the literature, this parameter depends on the type of heat treatment for which the material is submitted. It has been reported to anatase, for example, crystallite sizes of 18 nm and 25 nm, for TiO$_2$ thermally treated by muffle at 400°C during 5 or 6 hours [23,24]. The main morphological data are presented in Table 1. For an anatase synthesized by hydrothermal route (pH > 7 and 200°C, for 2h), a crystallite size equivalent to that estimated in the present study was reported [25]. This suggests that the presence of silica should have provided the composite with a significant reduction in the size of the crystallite, most likely due the suppression of the processes of growth and surface diffusion of the nanoparticles of TiO$_2$, partly due the curvature of the SiO$_2$ surface and formation of interfacial bonds between the oxides [26].

![Figure 1. Diffractogram obtained for the TiO$_2$/SiO$_2$ composite. The peaks indicated with “A” are attributed to the anatase phase of TiO$_2$ and “Al” refers to the sample holder (Aluminum).](image)

From the diffuse reflectance spectra, converted into Kubelka-Munk functions, and applying the direct method [27], Figure 2, it was possible to estimate the band gap energy ($E_g$) of the TiO$_2$ supported as being equal to 3.3 eV (Table 1).

| Photocatalyst | Crystallite size (nm) | Surface area (m$^2$g$^{-1}$) | Porosity (%) | Band gap (eV) | Ref |
|---------------|----------------------|-----------------------------|-------------|--------------|-----|
| TiO$_2$/SiO$_2$ | 10 | 70 | 15 | 3.3 | - |
| TiO$_2$-1 | 18 | 66 | 15 | 3.2 | 23 |
| TiO$_2$ | 25 | 55 | 12 | 3.2 | 24 |

*This study
For the commercial oxide TiO$_2$ P25, a mixture of anatase and rutile with about 70% anatase, the band gap energy ($E_g$) reported in the literature is around 3.2 eV [28,29], an equally reported value for pure anatase [23,24]. The slightly higher $E_g$ estimated for the synthesized composites may be related to a possible mixture of electronic states of both materials, highlighting that the amorphous silica possesses an $E_g$ higher than 8.0 eV [30].

![Graph](image1)

**Figure 2.** Diffuse reflectance spectra, expressed in terms of Kubelka-Munk function, for the (—) TiO$_2$/SiO$_2$ composite and (—)TiO$_2$ P25.

**Figure 3** presents the FT-IR spectra of the pure oxides (SiO$_2$ and TiO$_2$) and of the TiO$_2$/SiO$_2$ composite.

![Graph](image2)

**Figure 3.** Fourier Transform infrared spectra of (—) SiO$_2$, (—) TiO$_2$ and of the composite (—) TiO$_2$/SiO$_2$.

As observed, the pure SiO$_2$ presents three principal vibrations in the IR: a band centered at 438 cm$^{-1}$ related to Si-O-Si bending and the bands at 803 and 1050 cm$^{-1}$, respectively related to symmetric and asymmetric stretching of Si-O-Si. In addition to these bands, a secondary vibration related to Si-OH is observed at 960 cm$^{-1}$ [31-33]. For the pure TiO$_2$ three vibration characteristics are observed: a broad and intense band at 403 cm$^{-1}$ and more two subtle band at 530 and 730 cm$^{-1}$, both related to the Ti-O-Ti stretching [33,34]. Already for the TiO$_2$/SiO$_2$ composites, a band centered at 1102 cm$^{-1}$ can be observed in the region attributed to SiO$_2$ in addition to a band centered at 403 cm$^{-1}$, related to TiO$_2$. The Si-O-Si vibration (in general at 1050 cm$^{-1}$) is slightly shifted to higher frequencies (1102 cm$^{-1}$) due the calcination of the material at high temperature, suggesting the strengthening of this bond [33]. In all spectra it was possible to observe the occurrence of two relatively wide bands at 1636 cm$^{-1}$ and 3360 cm$^{-1}$ related to the vibration of O-H from H$_2$O molecules respectively chemisorbed and physisorbed on the surface of the photocatalyst [34,35]. It is important to note that in the IR spectrum of the composites bands were not observed in the range between 1350 to 1560 cm$^{-1}$, related to the presence of organic residues related to the precursor, attesting the effectiveness of the heat treatment to which the material was submitted after the synthesis [32,36].

In the N$_2$ adsorption/desorption assays using the BET (Brunauer-Emmett-Teller) method the isotherm obtained (**Figure S2**) is, according to IUPAC, classified as being type IV, characteristic of mesoporous solids with average pore diameter between 2 and 50 nm [7,37]. Besides, the specific surface area was estimated as being 70 m$^2$/g, with 15% porosity (**Table 1**) and a mean pore diameter of 2.14 nm, calculated using the BJH (Barrett-Joyner-Halenda) method. The oxides synthesized in previous studies [23,24], also using the sol-gel method, presented lower specific surface areas (66 and 55 m$^2$/g, respectively), suggesting that in the synthesis of TiO$_2$ the presence of SiO$_2$ may have favored the reduction of TiO$_2$ aggregation, increasing its surface area, since it is known that SiO$_2$ tends to restrict the mobility of TiO$_2$ crystals [26].

Images obtained by scanning electron microscopy are shown in **Figure 4**. Silica features particles slightly agglomerated with fairly regular spherical shape (**Figure 4a**). For the composites under study it is possible to observe an increase in the particle sizes, indicating the total covering...
of SiO₂ by TiO₂ (Figure 4b). In addition, it is possible to observe that there was the formation of TiO₂ outside the silica surface, possibly due to excess of precursor of titanium used in the synthesis. More images of SiO₂ and of the composite in other magnifications are available in the Supplementary Material (Figures S3 and S4).

Figure 4.

Photomicrographs for (a) SiO₂ and for the (b) TiO₂/SiO₂ composite.

2.2. Photocatalytic activity and hydrogen production

The evaluation of the photocatalytic activity of the synthesized composite was done on a bench scale, both by monitoring the discoloration of aqueous solutions containing the dye Ponceau 4R (P4R) and by the evaluation of the photocatalytic production of hydrogen.

Figure 5 shows the results obtained in photocatalytic tests of dye degradation using the composite TiO₂/SiO₂, quantified by monitoring the maximum absorbance of the dye at 507 nm. The decrease of P4R concentration follows an exponential decay profile as a function of the irradiation time, Figure 5 – Insert.

![Figure 5. Kinetics of discoloration of the dye Ponceau 4R (P4R) using the composite TiO₂/SiO₂ as photocatalyst. Insert: Absorbance reduction at 507 nm as a function of reaction time.]

The composite presented a good photocatalytic activity, with the elimination of 100% of the color of the dye in 140 minutes of reaction. This is due to the fact that the immobilization of titanium dioxide on the surface of silicon dioxide should have provided a better dispersion of the catalyst, thus avoiding the problems usually related to its aggregation [38,39]. It is well established that the degradation of organic matter, by heterogeneous photocatalysis, follows pseudo-first order kinetics [4, 40, 41]. Based on this premise, the kinetics was adjusted by linear regression of the data of the Neperian logarithm of the concentrations ratio, \(-\ln(C/C₀)\), versus reaction time, Figure 5. Based on this figure, the P4R degradation appears to occur in two stages. In the first 80 minutes of reaction the estimated value of the apparent rate constant is \(2.2 \times 10^{-2} \text{min}^{-1}\) (\(R^2=0.9912\)), increasing...
to 5.0 x 10^{-2} \text{ min}^{-1} (R^2= 0.9736) in the last 60 minutes, when the degradation rate practically doubles. This increase in the degradation rate can be explained by the relative growth of the number of reactive species produced by the photocatalyst throughout the process as the concentration of oxidable substrate decreases [42]. Comparatively, the estimated degradation rate of P4R mediated by the composite evaluated in this study is approximately 40% higher than the observed in the degradation of this same substrate in a photocatalytic reaction mediated by TiO_2 photocatalysts prepared by the Pechini method [43], and approximately close to that obtained using a TiO_2(P25)/ZnPc 1.6% composite, or a TiO_2 prepared by the Sol-gel method [43].

Regarding the production of hydrogen, a production of 5.5 mmol of H_2 was achieved in 5 hours of reaction. O advance of the reaction is shown in the following figure.

![Figure 6. Hydrogen production (mmol) as function of the reaction time using the composite TiO_2/SiO_2 as photocatalyst, with the addition of a charge of 0.05% m/m of Pt as cocatalyst.](image)

For comparative purposes, in addition to the amount hydrogen produced, the results also can be presented in terms of the specific rate of hydrogen production (SRHP), defined as:

$$SRHP = \frac{n}{t \cdot m}$$  \hspace{1cm} \text{Equation 1}

In which \(n\) is the number of mols of H_2 produced, obtained by integration throughout the experiment; \(t\) is the total reaction time and \(m\) is the mass of photocatalyst (in grams). The SRHP achieved using the composite was of approximately 13.6 mmol g^{-1}h^{-1}, a result much higher than that obtained using the commercial oxide TiO_2 P25 (2.66 mmol g^{-1}h^{-1}) under the same experimental conditions.

In tests using an association between TiO_2 (anatase) and ZnO, Xie and coworkers reached a SRHP of 2.15 mmol g^{-1}h^{-1}, but adding to the catalyst 0.5% m/m of Pt [44]. In another study, Zhu synthesized TiO_2 (anatase) over carbon nanospheres, carrying this material with Pt 0.1% m/m, achieving an SRHP of 2.85 mmol g^{-1}h^{-1}[45]. It should be noted that in both studies the experimental conditions were similar to those applied in the present study. Considering that these results were the most representative in the mentioned studies, it can be affirmed that the SRHP using the TiO_2/SiO_2 presented in this work is superior to the reported in these studies. It should be emphasized that the amount of cocatalyst used in this study is much smaller than in the reported studies.

In this way, it is observed that the silica coating by TiO_2 obtained by sol-gel synthesis resulted in a promising photocatalyst with excellent performance both in the degradation of P4R as catalytic production of hydrogen gas.

### 3. Material and Methods

Titanium dioxide supported in silicon dioxide was synthesized by the sol-gel method [46]. Prior to its preparation, the SiO_2 was synthesized using the Stöber method [47].

#### 3.1. Synthesis of SiO_2

15 mL of Milli-Q water and 4 mL of NH_4OH (28%, Synth) were added to 100 mL of ethanol (99.8%, Vetec). This mixture was maintained under magnetic stirring for 5 minutes and then 3 mL of tetraethyl orthosilicate (98%, Sigma-Aldrich) were quickly added. From there, the mixture was kept under vigorous stirring for over 1 hour. Finally, the solution was neutralized with 5M HCl solution (P.A., Biotec), centrifuged and dried in an oven at 70 °C for 15 hours.

#### 3.2. Synthesis of the composite TiO_2/SiO_2

0.2 g of dry silica were dispersed in 80 mL of
2-propanol (99.5%, Vetec), being this suspension maintained under magnetic stirring for 5 minutes. Then were added quickly 3 mL of titanium isopropoxide (97%, Sigma-Aldrich), being the mixture maintained under vigorous stirring for 19 hours. Following, using a procedure adapted from Santos et al [24], proceeded to the hydrolysis of the titanium isopropoxide, using a mixture containing 6 mL of 2-propanol and 3 mL of Milli-Q water, which was added slowly to the suspension. This mixture was then kept under magnetic stirring for 1 hour. Finally, the resulting colloidal suspension was centrifuged, and the precipitate was separated and submitted to calcination in muffle at 450 °C for 5 hours. By stoichiometric calculations, the proportion between the two oxides present in the synthesized composite is approximately 80% of TiO₂ and 20% of SiO₂.

3.3. Characterizations

A SHIMADZU XRD-6000 diffractometer coupled with a CuKα (λ= 1.54 nm) monochromatic source were used to evaluate the crystallinity of the composite and its crystalline phase, in the angular range between 10° ≤ 2θ ≤ 90°, with scanning speed of 2°min⁻¹. The measurements of electronic absorption by diffuse reflectance were performed using a SHIMADZU model 1650-PC spectrophotometer. The infrared spectra were acquired using a Perkin Elmer Frontier Total Attenuated Reflectance FTIR spectrometer. The measurements were done on a diamond crystal plate, using 16 scans with a resolution of 4 cm⁻¹, for each sample. Specific surface area measurements were performed using a Quantachrome model 2000 Surface Area, Pore Size and Distribution Analyzer. For the morphological analysis of the materials, a TESCAN Vega 3 Scanning Electron Microscope was employed.

3.4. Evaluation of the photocatalytic activity and hydrogen production

Photocatalytic assays of P4R degradation were performed using a photocatalytic reactor described in previous studies [43]. A 400 W high-pressure mercury lamp, without the protective bulb, was employed as a source of ultraviolet radiation. Despite its emission spectrum, that covers both the ultraviolet and visible portions of the electronic spectrum [28], only photons with E ≥ 3.2 eV are capable to excite the photocatalyst. The experimental conditions were an aqueous suspension (4L) containing 100 mg L⁻¹ of the photocatalyst and 125 mg of the dye (P4R or New Coccine, Dye content 75%, Sigma-Aldrich). The suspension was circulated and irradiated for 140 minutes. The degradation, evaluated in terms of discoloration of the solution, was monitored by spectrophotometric measurements using a SHIMADZU UV – 1201 spectrophotometer.

The hydrogen production assays were carried out employing 75 mg of the photocatalyst loaded with 0.05% m/m of Pt. Platinum, from a solution of chloroplatinic acid hexaïdrated in isopropanol, was photochemically reduced at the beginning of the photocatalytic process, by its addition in a mixture containing 600 mL of Milli-Q water and 150 mL of methanol, used as sacrificial reagent (20% v/v). The suspension contained in the reactor was submitted to constant stirring, being irradiated by a high-pressure mercury lamp of 400 W, without the protective bulb.

The reactor, of borosilicate glass, is equipped with a cooling system that involves the part that contains the reaction medium. This cooling system is connected to a thermostated bath adjusted to 15 °C. The whole process occurred under nitrogen atmosphere.

The quantification of the hydrogen gas produced was performed every 1 hour, employing a Perkin Elmer Clarus 580 gas chromatograph, containing a Porapak-N column and a molecular sieve, coupled to a thermal conductivity detector.

All Photocatalytic assays were performed on a lab scale.

4. Conclusions

TiO₂ nanoparticles were successfully synthesized on the surface of SiO₂ spheres, employing the sol-gel method, giving rise to composites of the type TiO₂/SiO₂. The results obtained, in the level of photocatalytic assays, especially regarding the production of gaseous hydrogen, suggest that the level of coating achieved ensured improved photocatalytic properties to the catalyst.
As verified in the characterizations, the presence of silica ensured a higher thermal stability to the anatase, the only phase formed during the synthesis, a reduction in the crystallite size of up to 150% and an increase in the specific surface area of approximately 6% compared to TiO₂ anatase obtained by Santos et al. [24]. It was also found that the band-gap energy of the synthesized oxide is slightly higher than that reported for the TiO₂ P25 [28-29] and for the oxides (anatase) synthesized by França et al. [23] and Santos et al. [24]. By IR and MEV measurements, the coating of the SiO₂ by TiO₂ was confirmed.

The TiO₂/SiO₂ presented a good photocatalytic activity in the degradation of Ponceau 4R, a dye used as a model of oxidative substrate, reaching 100% of degradation in 140 minutes. The degradation achieved, confronted with the results reported by Oliveira et al. [41] under similar experimental conditions, but using TiO₂ synthesized by the Pecchini method, was at least 40% more efficient.

Concerning the hydrogen production assays, the result obtained using the TiO₂/SiO₂ composites was significantly better than that obtained using TiO₂ P25 or even in the comparisons done with similar studies presented in the literature [42-43]. These results indicate that the catalysts presented in this study have high potential for application both in environmental photocatalysis and in the photocatalytic production of hydrogen.

**Supporting Information**

**Figures S1-S4**

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