Self-cleaning of SiO$_2$-TiO$_2$ coating: Effect of sonochemical synthetic parameters on the morphological, mechanical, and photocatalytic properties of the films

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**A R T I C L E   I N F O**

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- Sonochemistry
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- Morphology
- Hydrophobic surface
- Photocatalytic surface

**A B S T R A C T**

Among the different properties of the hydrophobic semiconductor surfaces, self-cleaning promoted by solar illumination is probably one of the most attractive from the technological point of view. The use of sonochemistry for nanomaterials’ synthesis has been recently employed for the associated shorter reaction times and efficient route for control over crystal growth and the management of the resulting material’s photocatalytic properties. Moreover, the sol-gel method coupled to sonochemistry modifies the chemical environment, with reactive species such as -OH and H$_2$O$_2$, which yield a homogeneous synthesis. Therefore, in the following investigation, the sol-gel method was coupled to sonochemistry to synthesize a SiO$_2$@TiO$_2$ composite, for which the sonochemical amplitude of irradiation was varied to determine its effect on the morphology and mechanical and self-cleaning properties. SEM and APM characterized the samples of SiO$_2$@TiO$_2$ composite, and while the micrographs indicate that a high ultrasonic energy results in an amorphous SiO$_2$@TiO$_2$ composite with a low rugosity, which was affected in the determination of the contact angle on the surface. On the other hand, FTR analysis suggests a significant change in both SiO$_2$-SiO and SiO$_2$-TiO$_2$ chemical bonds with changes in vibrations and frequency, corroborating an important influence of the sonochemical energy contribution to the hydrolysis process. Raman spectroscopy confirms the presence of an amorphous phase of silicon dioxide; however, the vibrations of TiO$_2$ were not visible. The evaluation of hydrophobic and self-cleaning properties shows a maximum of ultrasonic energy needed to improve the contact angle and rhodamine B (RhB) removal.

**1. Introduction**

The synthesis of mesoporous materials from nano-sized units constitutes a recent and attractive approach for preparing novel surfaces, specifically for the fabrication of self-cleaning, anti-corrosion for electronics applications [1]. Self-cleaning surfaces have been widely studied after discovering the “lotus effect”, which is defined by the formation of spherical drops of water that roll on across the surface and clean it [2,3]. Therefore, this kind of surface has low water adhesion due to low surface energy modifying the surface’s physical aspect or chemically modifying the surface energy [4]. This is related to extended surface microstructures, resulting in two different wetting states, called hydrophobic and superhydrophobic surfaces, characterized by a contact angle up to 90° and 150°, respectively a sliding angle below 10° [5].

In this context, silicon dioxide (SiO$_2$) and polymers such as Polydimethylsiloxane (PDMS) have been employed to improve the hierarchical micro/nanostructure’s wettability. The bonds of the SiO$_2$ chemical species have high bond energy and large bond angle, and the addition of CH$_3$ groups contained in PDMS the chains results in a hydrophobic character to the composite, which is reflected by lower surface energy and good hydrophobicity [6,7].

On the other hand, the use of the semiconductor oxide materials such as ZnO [8], TiO$_2$ [9], Fe$_2$O$_3$ [10], and CuO [11] enhance the self-cleaning, anti-corrosion, anti-reflective and magnetic properties of composite materials. Specifically, titanium dioxide (TiO$_2$) has attracted attention worldwide due to its unique physicochemical properties, low cost, and good chemical stability, which have made this compound the most studied material for photocatalysis [12,13].
The union of SiO$_2$ and TiO$_2$ is highly efficient due to its chemical inertness, transparency in the wavelength region where TiO$_2$ absorbs, high thermal and mechanical stability, and a low refractive index [14,15]. For that reason, research with this synergic union has been widely explored. Wu et al., for example, reported a modification of the SiO$_2$@TiO$_2$ composite on glass characterized by a contact angle of 107.9°, that when is irradiated with UV light, causes the contact angle to decrease substantially [16]. In a related report focusing on photocatalytic performance, Kitsou et al. published a core–shell of SiO$_2$@TiO$_2$ that exhibited an 88.54% degradation of organic aqueous pollutants 4-nitrophenol [17]. In most of the related reports, however, the synthesis methods require long and harsh conditions; particularly, it is noteworthy that calculation is usually required. Methods like spattering and laser ablation have the advantage of shorter times and crystallinity and size control, but the energy cost is still a limiting factor [18].

One of the most convenient synthetic techniques to obtain the composite is the sol–gel method, which is easier, cheaper, and allows the control of size and crystallinity. Nevertheless, the requirements are longer than those used in physical synthetic methods, and it is necessary to employ some hazardous solvents. On the other hand, the sonochemistry technique is considered a green energy-source method since the chemical conditions are less rigorous and times of reaction are shorter, presenting attractive additional advantages such as better control of morphology and size [19,20].

In this context, some coupled synthetic methods have been explored to look for synergetic effects and synthesize the SiO$_2$@TiO$_2$ composite [21]. Prasad et al., for example, synthesized TiO$_2$ by a sonochemistry-assisted sol–gel method and found the ideal conditions for the growth of the rutile phase as a function of the energy supplied [22]. There is no information on the sonochemistry excitation parameters involved in synthesizing the SiO$_2$@TiO$_2$ composite to the best of our knowledge. Previous reports indicate the synthesis of SiO$_2$–TiO$_2$ materials using different methodological approaches. For instance, Kapridaki et al. used a sol–gel method that yields a hydrophobic material with moderate photocatalytic activity [23]. Besides, Deng et al. fabricated the composite by the hydrolysis and condensation of PDMS [24]. Another report indicates the use of laser ablation for the synthesis of the composite. These methodological approaches present some drawbacks such as long reaction time (26 h), the need for thermal treatment, or high energy or vacuum demands [25].

Aiming for the sustainable fabrication of SiO$_2$–TiO$_2$ composites, we investigate the advantages of using sonochemistry. Therefore, in this work, we present a hybrid technique, a sol–gel method coupled to sonochemistry to synthesize the SiO$_2$@TiO$_2$ composite under different conditions. Our research’s primary purpose is to investigate the influence of irradiation’s amplitude on the composite’s physicochemical properties (morphology, mechanical and self-cleaning). We aim to improve the material properties of previous studies of our research group [21]. The amplitude of sonic power input was varied from 20% to 100% while maintaining cavitation constant (100%). Cavitation keeps constant to establish a relation between the morphology and energy, avoiding cavitation influence [26]. The SiO$_2$@TiO$_2$ composites were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transforms infrared spectroscopy (FTIR), Raman spectroscopy, and UV–Vis spectroscopy. The self-cleaning properties were evaluated using the contact angle’s determination and the degradation of rhodamine B (RhB) under UV-A irradiation.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich) and titanium isopropoxide (TTIP, 97%, Sigma Aldrich), Polydimethylsiloxane (PDMS, Sigma Aldrich), distilled water, absolute ethyl alcohol (EtOH, 98%, JT Baker), and oxalic acid (JT Baker) were used as precursors and solvents in the synthesis method.

2.2. SiO$_2$@TiO$_2$ composite synthesis

The synthesis of the SiO$_2$@TiO$_2$ coating was carried out following the procedure proposed by Rosales et al. [21]. Namely, mixing two solutions under sonochemistry irradiation using a UP200Ht equipment with a d14 sonotrode (Hielser Ultrasonic Technology). TEOS’s molar relation, absolute ethyl alcohol, distilled water, PDMS, TTIP, oxalic acid, and isopropyl alcohol was 1: 5:6: 5.5: 0.15: 0.05: 0.05: 0.05.

A sol of SiO$_2$, a solution of absolute ethyl alcohol, and distilled water was prepared and irradiated with the sonochemistry source (20 kHz, UP2000Ht) for 15 min at various amplitudes delivering different power values (conditions 1) but maintaining constants the cavitation at 100%, meaning that the energy supply will be constant throughout the synthesis process. Afterward, TEOS (98%, Sigma Aldrich, St. Louis, MO, USA) was added dropwise, and the mixture was sonochemically stirred for 3 min. Later, polydimethylsiloxane was added dropwise under continuous stirring for another 3 min.

The TiO$_2$ sol was prepared, by adding titanium isopropoxide (97%, Sigma Aldrich, St. Louis, MO, USA) dropwise to isopropyl alcohol (99%, Sigma Aldrich, St. Louis, MO, USA), under a nitrogen atmosphere and continuous stirring.

Finally, the titanium dioxide and the silicon dioxide sols were mixed, modifying the sonotrode working parameters “conditions 2” (see Table 1). Immediately after mixing, 10 mL of distilled water were added and mixed continuously with the conditions for 20 min. The resultant mixture was applied as a thin film coating to the corresponding supporting surfaces (glass and mortar) and dried at room temperature.

2.3. Physical characterisation

The materials under study’s microstructural features were examined by scanning electron microscopy using a JOE JSM-6060 LV equipped with a dispersive energy module (SEM/EDS) operating at 15 kV. The SiO$_2$–TiO$_2$ films’ rugosity was determined by atomic force microscopy (AFM) using a Bruker Dimension edge with Scan Assyst. The IR spectra were obtained using an IRAffinity-1S spectrophotometer equipped with the complement ATR in the range of 850–4000 cm$^{-1}$. The crystallinity of the SiO$_2$@TiO$_2$ composite was determined by Raman spectroscopy with the LabRAM HR equipment (Horiba Scientific), which used an NdYAG laser ($\lambda$ = 532 nm). The glass substrates’ optical transmittance coated with SiO$_2$@TiO$_2$ was measured with a UV Detective Plus XB-10 spectrophotometer at wavelengths ranging from 350 to 800 nm.

2.4. Self-cleaning evaluation

Self-cleaning assessment and contact angle measurements were carried out over mortar samples manufactured following the ASTM method C192/C192M [27]. Following this method, the sample of SiO$_2$@TiO$_2$ composite as a coating spread over a porous matrix.

The measurement of the coatings’ contact angle was carried out employing a dosage unit, producing drops of water (0.10 mL) in standard conditions. The measurement was performed before (0 h) and after (4, 26, 26 h) of UV irradiation (365 nm). The Image J software (Fiji) [28]

Table 1

| Sample (SiO$_2$@TiO$_2$) | Condition of sonochemistry | Condition of sonochemistry |
|-------------------------|--------------------------|---------------------------|
| M1                      | 30% A                    | 20% A                     |
| M2                      | 60% A                    | 20% A                     |
| M3                      | 60% A                    | 50% A                     |
| M4                      | 100% A                   | 80% A                     |

A: Amplitude
was employed to carry out the mathematical treatment.

On the other hand, the photocatalytic activity was evaluated using a 50 ppm of Rhodamine B (RhB) solution as a model pollutant [21]. The dye was applied in 3 standardized positions on the surface of the mortar. The samples were exposed to UV-A irradiation for 65 h using a UV reactor, equipped with an Electrolux lamp GSO3 positioned at a 5 mm distance from the sample and characterized by an emission peak wavelength of 365 nm and an intensity of 30 W.

2.5. Durability

The adherence test was executed following the ASTM 3359 standard test [21,29] to study the durability of the SiO$_2$@TiO$_2$ coatings. A grid of 1 mm $\times$ 1 mm with eleven cuts of 20 mm in length was marked on the mortar surface to perform these experiments. Later, a piece of three inches long of scotch tape was placed in the center of the grid and softly pressed with an eraser. The scotch tape was then removed from the opposite side of the application, forming a 180° angle [29].

3. Results and discussion

3.1. Morphological characterization

SEM analysis was carried out to explore the morphology of the SiO$_2$@TiO$_2$ composites, and the resulting micrographs are shown in Fig. 1. By using a 2500X magnification, it is possible to observe that Fig. 1(a-d) shows the different size and interparticle distances of the obtained composites. As can be seen, by inspection of this figure, a major amplitude percentage of the sonochemistry energy radiation during the synthesis (Fig. 1(d)) results in the smaller particle size when compared to those shown in Fig. 1(a) (minimum amplitude).

In this regard, Enomoto et al. reported the agglomeration of suspended TiO$_2$ particles due to ultrasound irradiation. The effect is attributed to Ti-O-Ti bonds’ formation by combining Ti-OH bonds resulting from water condensation and enhanced collision frequency between these particles in solution [30]. Therefore, consistent with our observation, a higher amplitude will yield a lower degree of agglomeration, see Fig. 1(a) to Fig. 1(d).

Fig. 2 shows the three-dimensional AFM images taken from the sample surfaces of SiO$_2$@TiO$_2$ coatings deposited on glass slides. The studied surfaces are all equal and have 1x1 $\mu$m in area. Although all the surface under study shows craters’ characteristic presence, continuous and homogeneous morphology can be seen in all samples. The surface profiles are shown in Fig. 2(a-d). On the other hand, it reveals that the SiO$_2$@TiO$_2$ samples are characterized by different roughness values, depending on the sonochemical amplitude parameter used in the synthesis method. The samples’ roughness values are shown in Table 2, and while the SiO$_2$@TiO$_2$-M3 was the composite with the largest roughness value (Ra = 1.99 ± 0.033 nm), the SiO$_2$@TiO$_2$-M1 sample showed the smallest corresponding value Ra = 1.03 ± 0.006 nm. The samples SiO$_2$@TiO$_2$-M2 and SiO$_2$@TiO$_2$-M4 with values of Ra of 1.68 ± 0.005 and 1.45 ± 0.003 nm respectively showed no dependence with the sonochemical amplitude employed.

According to the SEM and AFM analysis, TiO$_2$ particles could not be observed since the SiO$_2$-TiO$_2$ volume ratios affect the size and agglomeration of TiO$_2$ particles. Consistent with this interpretation, Arier et al. reported a decrease in size and agglomeration of TiO$_2$ particles when increasing the SiO$_2$-TiO$_2$ volume ratios. Furthermore, a related increase in roughness was also observed to be a consequence of the decrease in the SiO$_2$-TiO$_2$ volume ratio [31,32]. Despite these observations, it is essential to point out that dependence of the roughness of the SiO$_2$-TiO$_2$ composite with the amplitude of the applied sonochemical radiation has not been established. In this research, the volume ratios were constant, and the only variation in the synthetic method was the amplitude. Therefore, the roughness of the SiO$_2$-TiO$_2$ composite was modified with the variation of amplitude (sonochemical energy) due to the segregation of coalescence into smaller particles, as supported by SEM analysis.

Fig. 1. SEM micrographs of the SiO$_2$@TiO$_2$ coatings (a) M1, (b) M2, (c) M3, (d) M4.
samples. Copolymerization of PDMS molecules with the Si-OH groups

3.2. Chemical and structural characterization

It is interesting to note that the samples SiO$_2$-M1 and M4 showed signals less defined and intense. The sample SiO$_2$-M1, the 960 cm$^{-1}$ band intensity reflects the formation of the Si-OH groups from TEOS’s hydrolysis creates a small band located at 850 cm$^{-1}$, which increases with the amplitude of the sonochemical excitation signal applied during the synthetic process [34].

On the other hand, transmittance spectra are dominated by a strong and broad band located between 1260 cm$^{-1}$ and 950 cm$^{-1}$. This band is the integration of several SiO$_2$ associated signals and residual organic groups such as PDMS and EtOH. Due to the variation of the amplitude of the sonochemical excitation energy radiation, it is crucial to follow the signals’ evolution and shifts. Thus, it is essential to deconvolute the band in its different peaks or bands to assess each component’s effect. In this way, the band spreads between 875 cm$^{-1}$ and 970 cm$^{-1}$ corresponds to the overlap of various PDMS peaks and SiO$_2$-TiO$_2$ peaks.

The band’s deconvolution located between 1000 cm$^{-1}$ and 1250 cm$^{-1}$ of the FT-IR spectrum of the SiO$_2$@TiO$_2$ composite is shown in Fig. 4. The resulting peaks are assigned to hydrolyzed alkoxy groups of the Si-O-Si bonds; 1025 cm$^{-1}$, 1050 cm$^{-1}$, which corresponds to asymmetric stretching vibrations Si-O-Si and the band at 1150 to 1180 cm$^{-1}$ corresponding to cross-linked Si-O-Si [39,40]. For the SiO$_2$@TiO$_2$-M2 composite sample (Fig. 4 (b)), a significant shift in the band at 1025 cm$^{-1}$ was observed. This shift, however, was not observed in the other composites, but the intensity changes considerably in samples SiO$_2$@TiO$_2$-M1 and M4 (Fig. 4 (a) and (d)), an observation that suggests a larger presence of Si-O-Si bonds.

The deconvolution of the bands of the SiO$_2$@TiO$_2$ composites located at 870 cm$^{-1}$ and 980 cm$^{-1}$ (see Fig. 5) show four peaks. These signals correspond to the PDMS/SiO$_2$@TiO$_2$ interactions. The band at 900 cm$^{-1}$ corresponds to the Si-OH bonds of PDMS. This signal is difficult to distinguish due to the interference of ethanol. Residues of this solvent come from the dilution of the PDMS process. The band at 930 cm$^{-1}$ (Si-O-Ti) corresponds to the interaction of TiO$_2$-SiO$_2$ in the composite. The peak at 950 cm$^{-1}$ reflects the vibration of the silanol group of PDMS and the band at 960 cm$^{-1}$, the unpolymerized silica matrix, and Si-O-Ti bonds [41,42]. For the SiO$_2$@TiO$_2$-M1, the 960 cm$^{-1}$ band intensity ([Fig. 5(a)]) suggests a higher polymerization stage compared to the SiO$_2$@TiO$_2$-M2 composite (Fig. 5(b)), in which this band is intense, and the low intensity of the signal at 950 cm$^{-1}$ reflects the poor formation of

![Fig. 2. AFM analysis of the SiO$_2$@TiO$_2$ coatings a) M1, b) M2, c) M3, d) M4.](image-url)

| Table 2 | Rugosity of the SiO$_2$@TiO$_2$ coatings. |
|---------|-----------------------------------------|
| Sample (SiO$_2$@TiO$_2$) | Roughness (Ra, nm) |
| M1      | 1.03 ± 0.006                           |
| M2      | 1.68 ± 0.005                           |
| M3      | 1.99 ± 0.033                           |
| M4      | 1.45 ± 0.003                           |
Fig. 3. ATR-FTIR spectra in the region between 4000 and 650 cm$^{-1}$ of the SiO$_2$-TiO$_2$ composite.

Fig. 4. Deconvolution of the 1250 cm$^{-1}$-1000 cm$^{-1}$ band of the SiO$_2$@TiO$_2$ composites a) M1, b) M2, c) M3, and d) M4.
the Si-O-Ti bond. On the other hand, the Si-O-Si bonds Cn’s deficient polymerization is suggested for the SiO$_2$@TiO$_2$-M2 composite (Fig. 5 (b)), since the bands at 960 cm$^{-1}$ and 950 cm$^{-1}$ are characterized by high and low in intensities, respectively.

To further analyze the effects of sonochemical energy over the physicochemical properties of SiO$_2$@TiO$_2$ composite. Raman spectroscopy was carried out, and the recorded spectra of the coatings are shown in Fig. 6. The vibrational modes located at 492 and 528 cm$^{-1}$ correspond to the amorphous phase of SiO$_2$, attributed to the three and four-membered chains of silicon and oxygen [43,44]. As observed from the figure, the SiO$_2$@TiO$_2$-M2 and M3 coating have well-defined bands compared to M1 and M4. The vibrations of PDMS exhibited characterstics Raman shift at 1246, 1265, 850, 797 and 705 cm$^{-1}$ [45]. However, in the SiO$_2$@TiO$_2$-M4, these bands are less intense, attributed to high sonochemical energy use. Furthermore, characteristic vibrational modes of TiO$_2$ were not identified due to its content being lower than the quantity of SiO$_2$.

The resulting data of UV–Vis analysis of the SiO$_2$@TiO$_2$ coatings over study are shown in Fig. 7. The corresponding spectrum of a glass substrate with a transmittance of 91–90% changes as expected by covering the surface with SiO$_2$@TiO$_2$ coatings, decreasing the transmittance values to 88–89%, 92–90%, 84–83%, and 91–90% for M1, M2, M3, and M4 respectively. The SiO$_2$@TiO$_2$-M2 coating is the best as it shows the higher transmittance value. However, the SiO$_2$@TiO$_2$-M4 presents a 10% less transmittance than the uncoated glass. This change in transmittance performance suggests a morphological change related to the SEM and AFM analysis and to the sonochemical amplitude applied during the synthesis producing smaller particles that directly affect the
light coating interactions.

3.3. Self-cleaning evaluation and contact angle

The water contact angle of the SiO\textsubscript{2}@TiO\textsubscript{2} coatings over mortar samples before (0 h) and after (4, 26, and 65 h) exposure to UV-A irradiation were measured to assess the stability of the coatings under study (see Fig. 8). The SiO\textsubscript{2}@TiO\textsubscript{2}-M3 coating shows a higher contact angle, 121\degree, after 4 h of UV-A irradiation; however, the contact angle value’s stability was variable and reached a maximum at 26 h of UV irradiation and a minimum of 12\degree at 65 h. On the other hand, the M1 and M4 SiO\textsubscript{2}@TiO\textsubscript{2} coatings showed a contact angle of 115\degree and 118\degree respectively, and a decrease of up to 16–17\degree at 65 h under UV-A irradiation. These dynamics correspond to changes in the surface’s rugosity (Table. 2), indicating a maximum, which is reflected by a decrease in the contact angle.

The photocatalytic activity of the samples under study was evaluated by assessing Rhodamine B (RhB) discoloration. Fig. 9 shows the color degradation evaluation of RhB produced by the SiO\textsubscript{2}@TiO\textsubscript{2} coatings photocatalytic activity. Inspection of the data shows that the best performing coating is SiO\textsubscript{2}@TiO\textsubscript{2}-M3, with a maximum of 88% of color removal after 26 h.

The SiO\textsubscript{2}@TiO\textsubscript{2}-M4 coating, on the other hand, shows a lower dye removal behavior, reaching 33% after the same experimental time, since this coating was synthesized with a higher amount of sonochemical energy. Furthermore, SiO\textsubscript{2}@TiO\textsubscript{2}-M1 reaches 39% discoloration with lower sonochemical radiation energy. It can be suggested that this variable does not have a substantial effect on the photocatalytic activity of the resulting coatings due to the low presence of O–H bonds affecting the interactions with the RhB molecule and the surface.

Recent research published by Wang et al. points out that the photocatalytic degradation of RhB at 80 ppm with different SiO\textsubscript{2}@TiO\textsubscript{2} nanocomposites deposited on mortar samples can reach color removal values above 80% after 65 h. It is important to note that these authors did not synthesize the SiO\textsubscript{2}@TiO\textsubscript{2} coatings in-situ [46].

In any case, M2 and M3 SiO\textsubscript{2}@TiO\textsubscript{2} coatings show the best self-cleaning performance, with higher contact angles and color removal percentages of RhB. These samples were synthesized with a 20–60% and 50–60% of the amplitude of ultrasonic energy, respectively. The use of a higher (100% of amplitude) or lower (20% of amplitude) amount of ultrasonic energy does not seem to improve the self-cleaning properties, and therefore, this effect probably corresponds to changes in the availability of the SiO\textsubscript{2}-TiO\textsubscript{2} bonds as suggested by the FTIR analysis. Moreover, the Ra values of rugosity indicate a significant dependence with the photocatalytic activity, indicating a flex point where the low rugosity no longer propitiates the photocatalytic activity.

3.4. Adherence tests

Table 3 shows the results of the adherence test performed according to the ASTM 3359 test. The coating with a higher classification standard corresponded to the SiO\textsubscript{2}@TiO\textsubscript{2}-M3 coating followed by the SiO\textsubscript{2}@TiO\textsubscript{2}-M2 coating 4B and 3B classifications, respectively, the SiO\textsubscript{2}@TiO\textsubscript{2}-M4 coating, on the other hand, showed the lower classification (1B), corresponding to a 40% of removed coating, followed by the SiO\textsubscript{2}@TiO\textsubscript{2}-M1 sample with a 2B classification. According to the corresponding classification table, the last SiO\textsubscript{2}@TiO\textsubscript{2}-M1 and M4 coatings are not resistant to mechanical strain, which is consistent with the changes of morphology and the lower values of the roughness of AMP that were previously discussed.

After performing the adherence test, the hydrophobic and photocatalytic properties were re-evaluated on the coatings previously tested for adherence, and the results are shown in Table 4; inspection of the relevant data shows that the SiO\textsubscript{2}@TiO\textsubscript{2}-M2 and M3 coatings are characterized by a decrease in the contact angle and self-photocatalytic activity up to 11%. On the other hand, the SiO\textsubscript{2}@TiO\textsubscript{2}-M1 and M4 coatings showed a higher decrease in the self-cleaning evaluation and contact angle due to the partial coating remotion.

These results are consistent with the AFM analysis, where the roughness value of Ra is 1.03 and 1.45 nm, for the SiO\textsubscript{2}@TiO\textsubscript{2}-M1 and M4 samples, respectively, demonstrating a dependence of the morphology with the surface. The SiO\textsubscript{2}@TiO\textsubscript{2}-M3 coating, on the other
4. Conclusions

The SiO$_2$@TiO$_2$ composites were synthesized by sonochemistry assisted sol–gel method using different power of ultrasonic energy. A maximum of 80% amplitude was the optimal value for obtaining the best self-cleaning properties and durability of the coatings with an optimal rugosity compared to the other coatings surveyed. We also confirmed that the application of sonochemical energy fosters or promotes a homogeneous surface morphology and chemical bonds that enhance these properties. The use of low sonochemistry energy, on the other hand, produces a major cluster size of the composite. However, it does favor SiO$_2$-TiO$_2$ bond formation. High sonochemistry energy radiation was found to decrease the cluster’s size modify the morphology, affecting the composite’s rugosity. In this way, it was possible to assess a relationship between sonochemistry amplitude with morphology and self-cleaning properties, establishing a direct dependence of roughness with the amplitude of the sonochemical stimulus during the synthesis process.

Therefore, the sonic amplitude was found to play a significant role in modifying the morphology and self-cleaning properties. As far as the synthesis of SiO$_2$@TiO$_2$-M3 is concerned, the process using 50% – 60% amplitude was the best one, as reveals from the high yields and homogeneous morphology obtained from the SEM and AFM experiments. This observation was further supported by durability and self-cleaning properties characterized by a 112° of contact angle, 88% of RhB color removal after 65 h, and a classification of 4B in the adherence test.

Further studies are needed to understand the chemical and morphological effects of the sonochemical energy in the SiO$_2$@TiO$_2$ composite, such as changes in the SiO$_2$:TiO$_2$ molar ratio, crystalline quality, and phase of the TiO$_2$.

Author contributions

K. Esquivel conceived and designed the experiments; Luis A. Godínez, L. Ortiz-Frade, and I. Medina characterized the samples by SEM, ATR-FTIR, and AFM techniques; A. Rosales synthesized the samples and collected and analyzed the data. All authors discussed the experiment results and contributed to the writing of the paper. All authors have read and agreed to the published version of the manuscript.

CRediT authorship contribution statement

A. Rosales: Conceptualization, Data curation, Formal analysis, Investigation, Methodology. L. Ortiz-Frade: Formal analysis, Resources, Supervision, Validation, Writing - original draft, Writing - review & editing. Iliana E. Medina-Ramirez: Formal analysis, Resources, Supervision, Validation, Writing - review & editing. Luis A. Godínez: Formal analysis, Resources, Supervision, Validation, Writing - review & editing. K. Esquivel: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 3

| Coating | % of the area removed | Imagen | ClassificationASTM D33-59-02 |
|---------|-----------------------|--------|-------------------------------|
| M1      | 30%                   | 2B     |                               |
| M2      | 10%                   | 3B     |                               |
| M3      | 5%                    | 4B     |                               |
| M4      | 40%                   | 1B     |                               |

Table 4

| Coating | Contact angle decrease (%) | Rhodamine B removal decrease (%) |
|---------|-----------------------------|---------------------------------|
| M1      | 28.8                        | 30                              |
| M2      | 8.7                         | 10                              |
| M3      | 11.8                        | 5                               |
| M4      | 46.9                        | 40                              |
