

## Research Article

# SiO<sub>2</sub>-TiO<sub>2</sub> Films Supported on Ignimbrite by Spray Coating for the Photocatalytic Degradation of NO<sub>x</sub> Gas and Methyl Orange Dye

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In this work, a SiO<sub>2</sub>-TiO<sub>2</sub> coating, composed of different numbers of TiO<sub>2</sub> and SiO<sub>2</sub> layers, was fabricated by a spray-coating technique. The films were deposited onto ignimbrite rock and divided into two groups according to the number of SiO<sub>2</sub> layers applied, 10 and 15 layers of SiO<sub>2</sub> and 5 layers of TiO<sub>2</sub> for each group. The morphology and chemical composition of the synthesized samples were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometer (EDS), which reveal the successful SiO<sub>2</sub>-TiO<sub>2</sub> coating on ignimbrite. The photocatalytic activities of samples obtained were evaluated toward the decomposition of 3 ppm of methyl orange (MO). Finally, NO<sub>x</sub> gas degradation was studied. The obtained results evidenced that the SiO<sub>2</sub> and TiO<sub>2</sub> coating improved the photocatalytic activity of ignimbrite.

## 1. Introduction

In Peru, there are few studies on mitigating damage to rocks belonging to architectural monuments. However, in the city of Lima, Gallarday [1] studied the deterioration of various churches in the historic center of the city and made a financing proposal for the preservation and restoration of the main ornamental rocks. In Arequipa, the most important study was carried out in 2006 [2] by the Ministry of the Environment, in which the main agents and mechanisms of alteration of the rocks (ignimbrite) belonging to the historical monuments of Arequipa were determined. Thanks to this study, the concern for the improvement of the historic center of Arequipa city began, seeking effective and simple solutions or alternative that allows the protection, self-cleaning, and preservation of the cultural heritage. In this aspect, the use of nanomaterials begins to gain importance to achieve the

desired improvement. Zornosa-Indart et al. [3, 4] used silica-based inorganic hybrid nanomaterials that improve robustness, hydrophobicity, and resistance and consolidate limestone rocks significantly, in order to achieve the conservation of the cultural heritage. Additionally, the use of titanium dioxide (TiO<sub>2</sub>) photocatalyst in the improvement of the facades of historic buildings has been studied with good results [5, 6] and in combination with cementitious and other construction materials has shown a favorable synergetic effect in the removal of air pollutants [7, 8]. Thus, the researches continued and led to the implementation of a system based on silica as a support material and TiO<sub>2</sub> nanoparticles as a photocatalyst material [9–11]. Nevertheless, the use of a silicon-titanium hybrid system in the degradation of methyl orange (MO) dye and NO<sub>x</sub> gases on ignimbrite surfaces has not yet been reported. Therefore, the aim of this work is to carry out a study on a TiO<sub>2</sub>-SiO<sub>2</sub> coating system,



FIGURE 1: Photographs of (a) ignimbrite, (b) 10TEOS-5TiO<sub>2</sub>, and (c) 15TEOS-5TiO<sub>2</sub> samples.

composed of different numbers of layers of SiO<sub>2</sub> and TiO<sub>2</sub> achieved with the spraying coating technique. These coatings could protect the cultural heritage of the city of Arequipa, Peru, from organic and air pollutants. Detailed morphological characterization of samples was investigated by field emission scanning electron microscopy (FE-SEM). Then, methyl orange dye degradation measurements will be previously performed in order to determine the effectiveness of the coating systems. Finally, we will evaluate the NO<sub>x</sub> gas elimination capacity in a laboratory gas analyzer.

## 2. Experimental

**2.1. Synthesis of the Sols.** All reagents used in the experiments were of analytical grade and used without any further purification. The TiO<sub>2</sub> and SiO<sub>2</sub> sols were prepared, respectively, according to Arconada [12] and Reyes et al. [13]. The TiO<sub>2</sub> sol was obtained from the mixture of 49.5426 g of ethanol, component used as solvent of the sol-gel process with 1.6140 g of acetic acid and 7.8758 g of titanium isopropoxide (TTIP), where TTIP is the main component of titanium precursor. Then, 0.9676 g of water acidified with hydrochloric acid (HCl, 0.1 N), that acts as the catalyst for the solution, was added dropwise, and the whole mixture was stirring for 1 hour until dissolved. Meanwhile, the preparation of the silica sol (SiO<sub>2</sub>) was prepared from the precursor tetraethy-

lorthosilicate (TEOS), dissolving 40.602222 g of TEOS in 105.63776 g of ethanol. Then, 3.4384 g of water acidified with 0.1 N hydrochloric acid was added dropwise; the mixture was stirring at 60°C in a cooling bath with glycerin at 11°C for a period of 90 minutes. After that time, the temperature was reduced to 40°C and 10.31536 g of acidified water was added dropwise again. Finally, the solution was left under stirring for a period of 60 minutes in the cooling bath.

**2.2. Deposition of the Coatings.** The coating of ignimbrite employing TiO<sub>2</sub> and SiO<sub>2</sub> sols was carried out by a spray-coating technique, using a set of airbrushes with fluid control at a distance of 5 cm from the ignimbrite. SiO<sub>2</sub> and TiO<sub>2</sub> layers were obtained by calcination at 450°C for 30 minutes and 60 minutes, respectively, at a heating rate of 10°C/min. Two groups of samples were fabricated according to the number of layers of TiO<sub>2</sub> and SiO<sub>2</sub> applied. The first group of samples was fabricated with 10 layers of SiO<sub>2</sub> and 5 of TiO<sub>2</sub> and labelled as 10TEOS-5TiO<sub>2</sub>, whereas the second group was fabricated with 15 layers of SiO<sub>2</sub> and 5 of TiO<sub>2</sub> and labelled as 15TEOS-5TiO<sub>2</sub>.

**2.3. Characterization of the Samples.** The morphologies of obtained samples were visualized by a field emission scanning electron microscope (FESEM, Hitachi Regulus 8230) equipped with an energy dispersive X-ray spectrometer

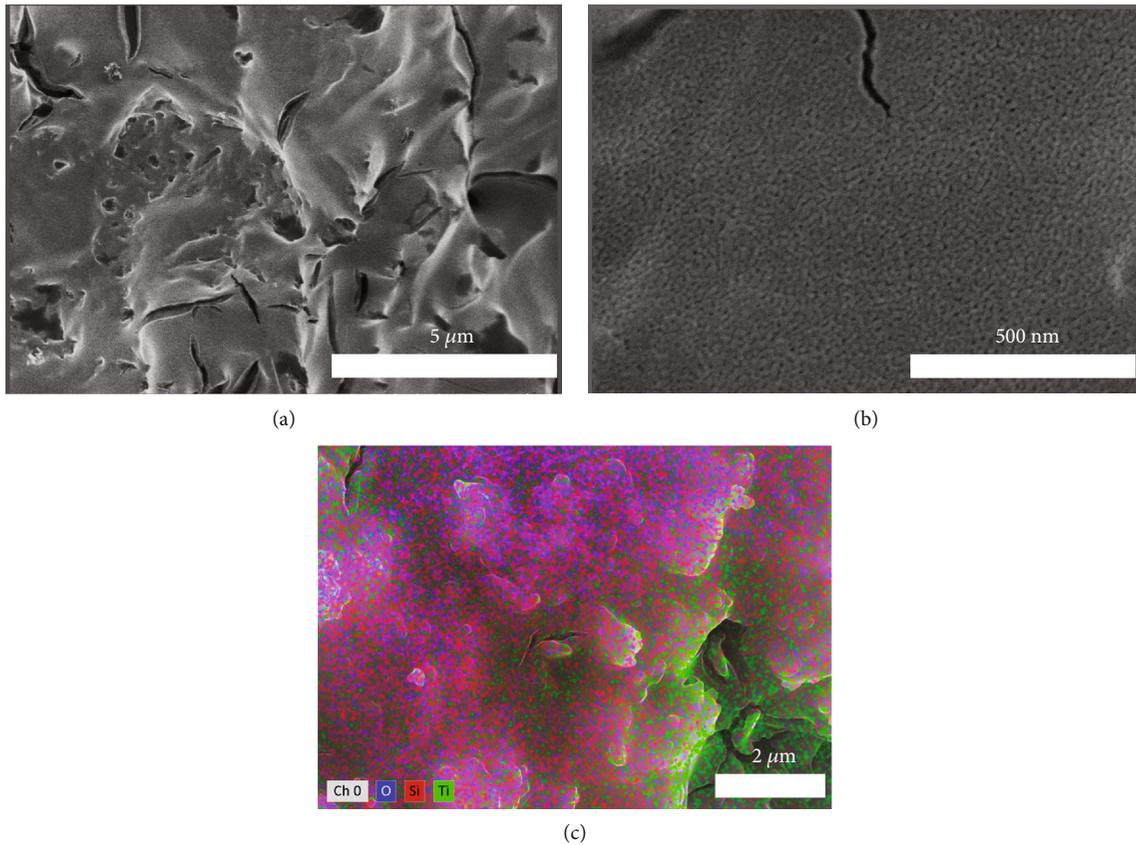


FIGURE 2: FE-SEM images of 15TEOS-5TiO<sub>2</sub> samples at magnification of (a) 10 KX and (b) 80 KX. (c) EDS element mapping image.

(EDX). The photocatalytic activities of the fabricated nanostructures were evaluated by the degradation of methyl orange (MO) under UV light irradiation, using a light source which simulates solar radiation (Newport 50-500 W). The next step was NO<sub>x</sub> gas mitigation monitoring (NO+NO<sub>2</sub>) performed with a chemiluminescence analyzer AC-32 M, Environment S.A., following the guidelines of ISO 22197-1: 2007. The NO<sub>x</sub> degradation efficiency was calculated using

$$\%NO_x = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100, \quad (1)$$

where  $[NO_x]_{in}$  is the initial NO<sub>x</sub> concentration (before turning on the UV source) and  $[NO_x]_{out}$  is the concentration at the end of the illumination period.

The photocatalytic activity and NO<sub>x</sub> degradation of 10TEOS-5TiO<sub>2</sub> and 15TEOS-5TiO<sub>2</sub> samples fabricated by a spray-coating technique were compared.

### 3. Results and Discussion

Figure 1 shows a photograph of ignimbrite, 10TEOS-5TiO<sub>2</sub>, and 15TEOS-5TiO<sub>2</sub> samples. Figure 1(a) is clearly to see the variety of porosity and minerals that conform the ignimbrite, unlike in Figure 1(b) where a whitish color is visualized covering the surface of the rock. In Figure 1(c), the intensity of this color increases and we obtained better compaction of the minerals present in the ignimbrite, an important require-

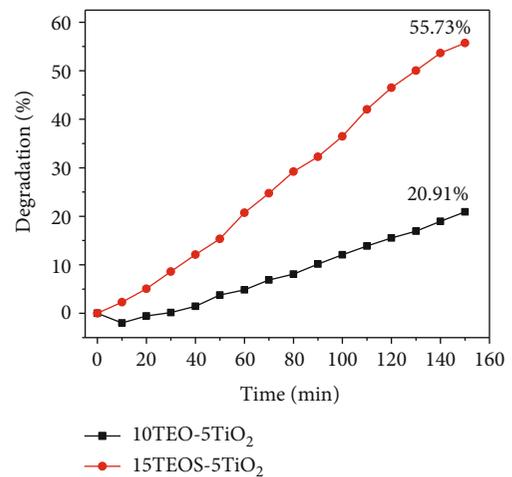


FIGURE 3: Photodegradation curves of methyl orange with different photocatalyst: 10TEOS-5TiO<sub>2</sub> (black line) and 15TEOS-5TiO<sub>2</sub> (red line).

ment to be applied on rocks of historical monuments for restoration [14].

The FE-SEM images obtained by field emission scanning electron microscopy of 15TEOS-5TiO<sub>2</sub> samples fabricated by spray coating at magnifications of 10 KX and 80 KX are shown in Figures 2(a) and 2(b), respectively. As shown in the figures, TiO<sub>2</sub> layers formed by nanoparticles can be seen in the top

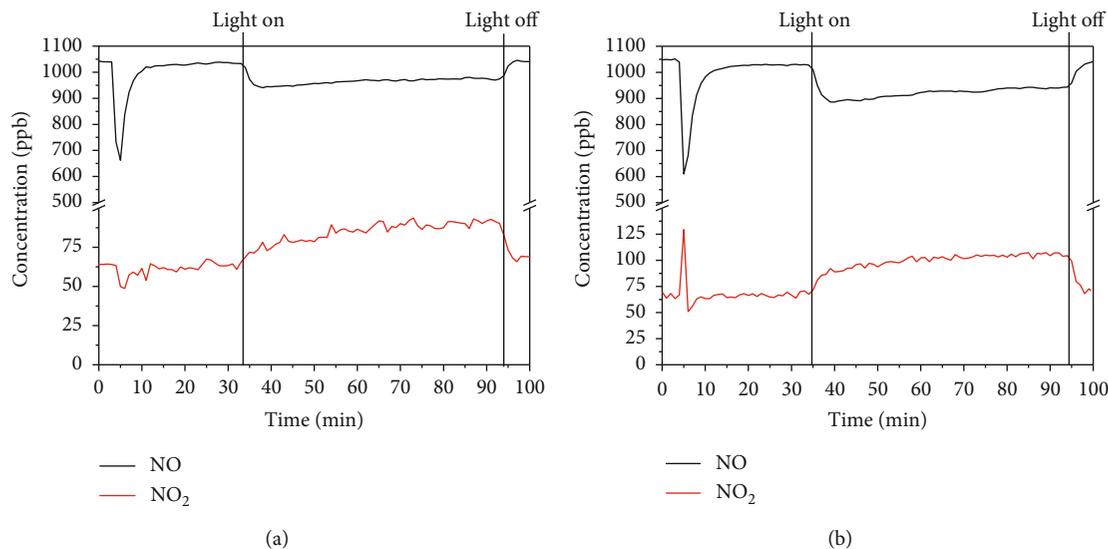


FIGURE 4: NO and NO<sub>2</sub> concentration during the test according to ISO 22197:1 2007 for (a) 10TEOS-5TiO<sub>2</sub> and (b) 15TEOS-5TiO<sub>2</sub> samples.

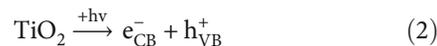
of the ignimbrite. Moreover, the EDS element mapping image in Figure 2(c) reveals the presence of titanium (Ti, green), silicon (Si, red), and oxygen (O, blue) elements, proving the coating of SiO<sub>2</sub> and TiO<sub>2</sub> layers on the surface of the ignimbrite.

In order to elucidate the effects of coating with TiO<sub>2</sub> and SiO<sub>2</sub> layers on the ignimbrite, the photocatalytic dye degradation performances of the 10TEOS-5TiO<sub>2</sub> and 15TEOS-5TiO<sub>2</sub> were evaluated in aqueous solution of methyl orange dye under UV-A irradiation. Figure 3(a) shows the change in the methyl orange concentration in aqueous solution in the presence of all samples. As shown, methyl orange molecules were not completely decomposed during 150 min of photocatalytic reaction. However, it was noted that 15TEOS-5TiO<sub>2</sub> photocatalyst shows the highest photocatalytic activity compared with 10TEOS-5TiO<sub>2</sub> photocatalyst. The degradation efficiency of the 15TEOS-5TiO<sub>2</sub> photocatalyst shows a maximum degradation of ~55.73% at 150 min, whereas the degradation efficiency of 10TEOS-5TiO<sub>2</sub> was ~20.91% at the same irradiation time. The enhancement of photocatalytic efficiency must be attributed to the increase in the number of SiO<sub>2</sub> layers, which achieve better support for the coating of TiO<sub>2</sub> [15]. Thus, having more TiO<sub>2</sub> exposed directly the photocatalytic efficiency which could be improved, having a better performance in the degradation of the methyl orange dye.

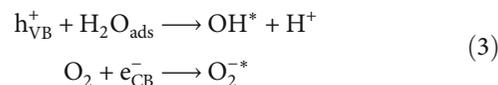
The chemiluminescence analysis for the variation of the concentration of NO and NO<sub>2</sub> in parts per micromolar is shown in Figure 4. An appropriate amount of the SiO<sub>2</sub>-TiO<sub>2</sub>-coated ignimbrite was loaded into the reactor, and then, the reactor was carefully sealed. Afterwards, the NO containing nitrogen gas and the purified air were allowed to flow into the reactor at flow rates of 3 L/min each, until equilibrium NO<sub>x</sub> concentration in the inflow was achieved (1000 ppb). The evaluation of photocatalytic activity was 1 hour at 10 W/m<sup>2</sup> with 35 minutes of saturation of the rock in the dark. In the first 30 minutes in the dark, the peaks observed in the graphs are the flow of gas entering the cham-

ber, so it has no influence on the measurements. After the one hour of irradiation, the light source was turned off and then the gas valves were closed. All experiments were conducted at ambient temperature (25 ± 3°C). The detailed experimental procedure can be referred to published literatures [7, 8] and the ISO 22197-1 : 2007 standard of air purification performance of semiconductor photocatalytic materials [7]. Figure 4(a) shows a slight increase in NO<sub>2</sub> production for the 10TEOS-5TiO<sub>2</sub> substrate, which causes a greater amount of NO<sub>x</sub> removal. In the case of the gaseous medium, a better degradation result of 0.80 μmol was obtained, which translates into 15.95%, whereas the obtained degradation for 15TEOS-5TiO<sub>2</sub> substrate, shown in Figure 4(b), was 0.63 μmol, which is equivalent to 10.56%. According to the reports [16, 17], the NO<sub>x</sub> gas degradation phenomena are mainly due to the presence of TiO<sub>2</sub> in our samples.

It is important to know the mechanism of heterogeneous photocatalytic degradation of NO<sub>x</sub> gases by TiO<sub>2</sub>. These processes are summarized in the following reactions for the 10TEOS-5TiO<sub>2</sub> and 15TEOS-5TiO<sub>2</sub> samples as photocatalytic materials. When the nanostructure is irradiated from the light source, the electrons (e<sup>-</sup>) in the valence band (VB) are excited to the conduction band (CB) with generation simultaneous of the same number of holes (h<sup>+</sup>) in the VB (Equation (2)).

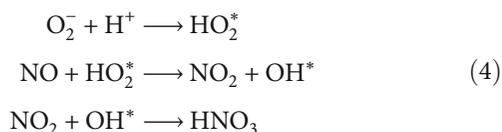


The reaction of the H<sup>+</sup> with the OH<sup>-</sup> is dissociated from the water to form the OH\* [18–20] and the reaction with the electrons with the O<sub>2</sub> to form a superoxide anion O<sub>2</sub><sup>-</sup> [20, 21].



Then, the reaction of O<sub>2</sub><sup>-\*</sup> with H<sup>+</sup> from water produces HO<sub>2</sub><sup>\*</sup> radicals; NO diffusion occurs on the surface of TiO<sub>2</sub>

and forms  $\text{NO}_2$ . Finally,  $\text{NO}_2$  reacts with hydroxyl radicals forming nitric acid:



#### 4. Conclusions

In summary,  $\text{SiO}_2$  and  $\text{TiO}_2$  coatings on ignimbrite were achieved by a spray-coating technique, varying the number of  $\text{SiO}_2$  layers in 10 and 15 layers, while the number of  $\text{TiO}_2$  layers remained constant at 5 layers. The photocatalytic activities of the samples obtained were evaluated toward the decomposition of methyl orange (MO) and  $\text{NO}_x$  gas degradation. The obtained results evidenced that the  $\text{SiO}_2$  improved the porosity of ignimbrite, whereas the  $\text{TiO}_2$  coating improved the photocatalytic activity. The enhancement in the photocatalytic activity of the  $\text{SiO}_2$ - $\text{TiO}_2$  hybrid system is attributed to the high efficiency in both light utilizations, the higher transfer rate of photogenerated electrons from  $\text{SiO}_2$  to  $\text{TiO}_2$  and repressed recombination of the photoinduced hole-electron pairs of  $\text{TiO}_2$ , which is closely related to the chemical interaction between  $\text{TiO}_2$  and  $\text{SiO}_2$ .

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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