

Influence of Temperature on the Photocatalytic Activity of Sol–Gel TiO₂ Films

Stefano Costacurta,[†] Gabriele Dal Maso,^{†,‡} Riccardo Gallo,^{†,‡} Massimo Guglielmi,[‡] Giovanna Brusatin,[‡] and Paolo Falcaro^{*,§}

Associazione CIVEN, Via delle Industrie 5, 30175 Venezia, Italy, Dipartimento di Ingegneria Meccanica Settore Materiali, Università di Padova, Via Marzolo 9, 35131 Padova, Italy, CSIRO Materials Science & Engineering, Gate 5 Normanby Road, Clayton VIC 3168, Australia

ABSTRACT The photocatalytic activity of TiO₂ films synthesized via the sol–gel process has been measured as a function of UV irradiation time and substrate temperature. Fourier-transform infrared spectroscopy has been used to address the chemical changes in stearic acid and block copolymer Pluronic F127 films deposited on the photocatalytic surface. When the temperature of the photocatalytic substrate was raised above 50 °C, the removal of stearic acid from the surface was strongly affected by a process involving evaporation, whereas Pluronic F127 revealed a superior stability. Our study shows that heat enhances the photocatalytic activity, suggesting the importance of an accurate temperature control in photocatalytic efficiency measurements.

KEYWORDS: photocatalysis • titanium dioxide • stearic acid • block copolymer • Pluronic F127 • Fourier transform infrared spectroscopy

INTRODUCTION

Photocatalytic activity is based on the formation of a photogenerated electron–hole pair upon absorption of a UV photon; photocatalysis involves holes oxidizing the adsorbed organic species and electrons reducing the hydroxyls adsorbed on the surface to OH· radicals, which in turn act as oxidizing agents toward organic species producing simpler byproduct such as CO₂ and H₂O. Thus, the organic species deposited on a photocatalytic surface can be decomposed upon UV illumination (1, 2). The photocatalytic property of titanium dioxide (TiO₂) in its crystalline anatase phase is exploited in devices for air and water purification, self-cleaning, and antibacterial coatings (3, 4).

Heat, generated either by the UV lamp or by an external source, influences the reaction pathways and the kinetics of the organic degradation process; this is a central aspect in applications where the substrate temperature can be varied in order to attain better performances, e.g., in purification and sterilization devices and in household appliances. In the studies dealing with the effect of temperature on photocatalysis, the temperature effect is considered chiefly from a phenomenological point of view or is disregarded (4–6). Photocatalysis has been measured in systems based on TiO₂ particles suspended in supercritical fluids (7), fluidized-bed reactors (8), membranes for air purification (9), and reactors for water purification (10); in these reports, the decomposition of small organic molecules (octanol, chlorobenzene, an

azo dye, and formaldehyde, respectively) was studied varying operating parameters such as pressure or gas flow and temperature. However, in all of these reports, the contribution of photocatalytic activity is not differentiated from other thermal effects; furthermore, these systems are based on particulate TiO₂ and none focuses on coatings. Remarkably, no distinction is made between organic degradation by the photocatalytic substrate and other effects, such as evaporation and degradation induced by the direct UV radiation on the organic material. A systematic study regarding the degradation of ethylene using a fixed-bed tubular reactor was published by Fu et al. (11). Only one work deals with a photocatalytic planar surface, focusing on the degradation of ethylene as a function of moisture and temperature (12). However, the degraded organic molecule is small and in the gas phase; furthermore, only temperatures lower than 50 °C are considered. These works present studies on the kinetics and there is a general lack of a standard protocol for testing photocatalytic coatings based on the spectroscopic characterization of the UV–temperature combined effects.

In this letter, we report the results of the measurement of photocatalytic efficiency in sol–gel TiO₂ films when the substrate temperature is varied. In experiments at ambient temperature, stearic acid (CH₃(CH₂)₁₆COOH) is typically used as a sacrificial organic coating (13). However, when measurements are performed at higher temperatures (50 < *T* < 100 °C), a different organic substance should be employed. In fact, for temperatures higher than ~50 °C, stearic acid is subject to significant evaporation and/or degradation. Block copolymer Pluronic F127 revealed better qualities as a sacrificial organic molecule for testing the photocatalytic properties of a sol–gel TiO₂ film at high temperature. A spectroscopic investigation comparing the two organic mol-

* To whom correspondence should be addressed. E-mail: paolo.falcaro@csiro.au.

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[†] Associazione CIVEN.

[‡] Università di Padova.

[§] CSIRO Materials Science & Engineering.

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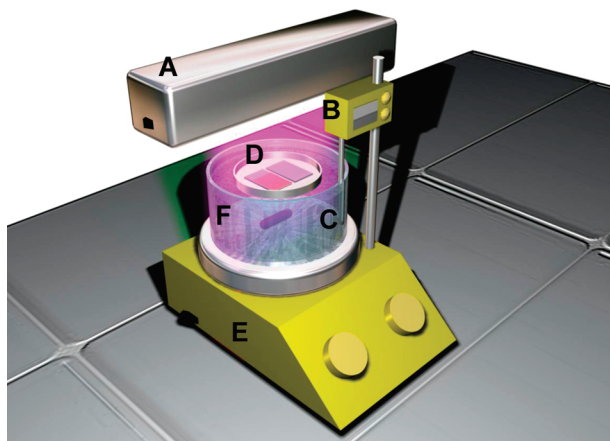


FIGURE 1. Experimental setup used for the UV irradiation of samples at constant temperature. (A) UV lamp; (B) temperature controller; (C) thermocouple; (D) sample; (E) magnetic stirrer/heater; (F) thermostatted oil bath.

ecules is presented in this paper. The study of this thermal effect should increase the understanding of the processes involved in photocatalysis and represents a technological advantage for more efficient self-cleaning devices.

RESULTS AND DISCUSSION

The TiO_2 coatings in their anatase (photocatalytic) crystalline form were obtained via the sol-gel process using titanium tetraisopropoxide (TTIP) as the Ti source, as de-

scribed in the Supporting Information. A sacrificial organic coating (either stearic acid or Pluronic F127) was deposited on the substrates by spinning an alcoholic solution, and the films were then irradiated with UV light (see the Supporting Information for details) for selected time intervals, acquiring a FTIR spectrum of the sample at each interval. The photocatalytic efficiency curves were obtained integrating the area of the C-H vibrational band between 3000 and 2700 cm^{-1} in the FTIR spectra taken at different UV exposure times (14). The substrate was in contact with a metal plate thermostatted with a silicone oil bath (Figure 1) in order to ensure constant temperature. The samples were kept in the dark both before and after UV exposure, and the whole experimental apparatus was enclosed in a dark cabinet in order to avoid possible degradation effects due to external light.

When stearic acid was used to monitor the photocatalytic activity of TiO_2 films at different temperatures, a decrease of the organic content was observed at $75\text{ }^\circ\text{C}$ even when stearic acid was deposited on a nonphotocatalytic Si substrate (Figure 2 a–c). The same behavior was observed both with and without UV illumination. This phenomenon can be explained by evaporation of stearic acid (melting point $69.6\text{ }^\circ\text{C}$) (15); the support to this conclusion is provided by the observation that in the FTIR spectra the C-H ($3000\text{--}2800\text{ cm}^{-1}$ range) and carbonyl ($\text{C}=\text{O}$, 1740 cm^{-1}) bands decrease at the same rate. We have integrated the CH and C=O band areas and the ratio between these two bands ($A_{\text{C-H}}/A_{\text{C=O}}$)

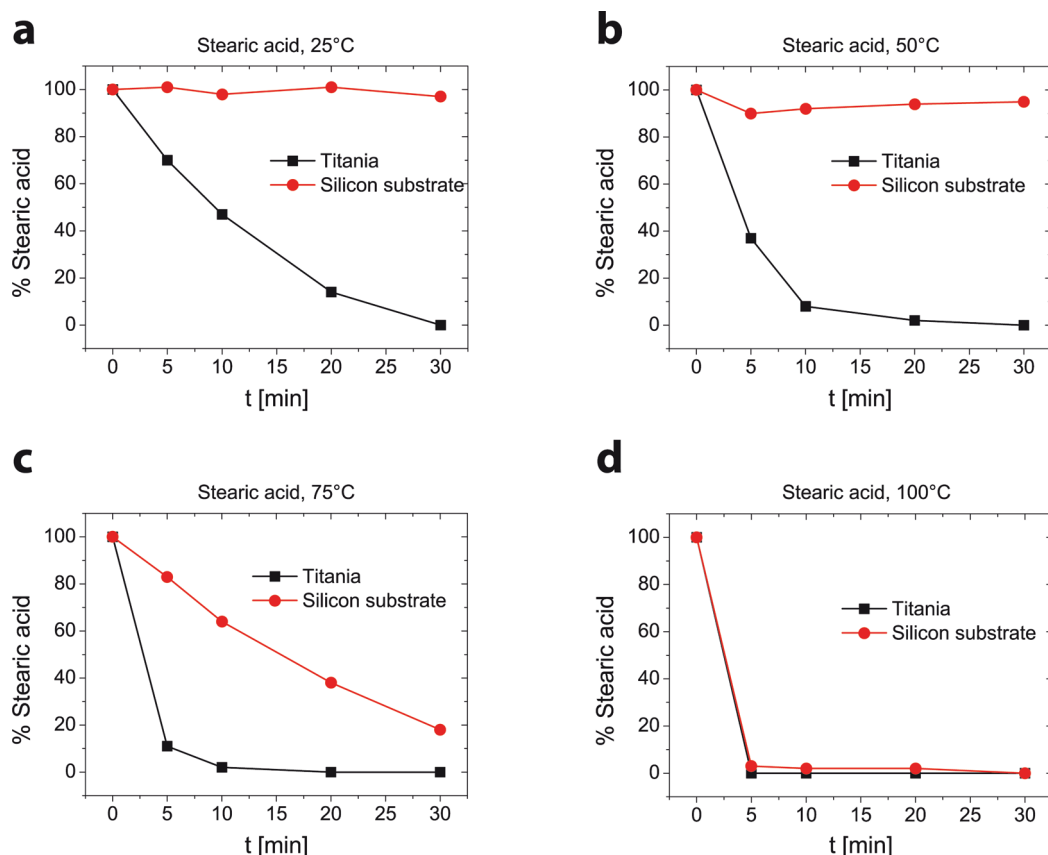


FIGURE 2. Percentage of stearic acid, deposited on bare Si and on TiO_2 -coated substrates, remaining on the surface upon UV exposure at different temperatures and times. The values were obtained integrating the C-H bands ($3000\text{--}2800\text{ cm}^{-1}$ range) of the FTIR spectra. The lines are a guide for the eyes.

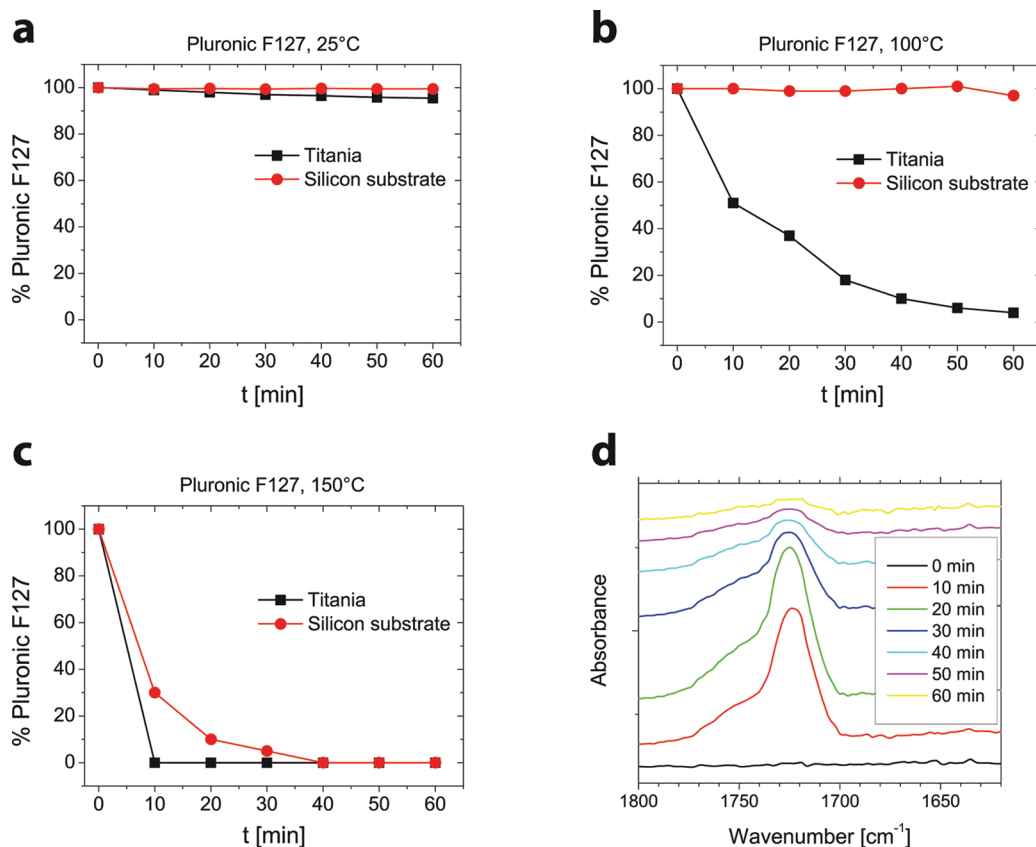


FIGURE 3. (a–c) Percentage of Pluronic F127, deposited on bare Si and on TiO_2 -coated substrates, remaining on the surface upon UV exposure at different temperatures and times. The values were obtained integrating the C–H bands ($3000\text{--}2800\text{ cm}^{-1}$ range) of the FTIR spectra (the lines are a guide for the eyes). (d) FTIR spectra of Pluronic F127 deposited on TiO_2 -coated substrates and UV irradiated at $100\text{ }^\circ\text{C}$ for different times, showing the region of the carbonyl groups ($\sim 1740\text{ cm}^{-1}$).

was found to remain constant with time. Therefore, we conclude that no carbonyl formation is observed, i.e. no oxidation occurs in these conditions (see the Supporting Information, Figure S2a). On the other hand, in stearic acid films deposited on TiO_2 and UV irradiated for 10 min at $25\text{ }^\circ\text{C}$, the decrease in the C–H band occurs more rapidly than the decrease of the C=O band and the ratio $A_{\text{C-H}}/A_{\text{C=O}}$ was found to decrease with UV exposure time. This behavior was attributed to photocatalytic oxidation of the stearic acid film, causing formation of decomposition products containing carbonyls (Figure S2b). This leads to the conclusion that caution should be used in the interpretation of data when stearic acid is used in the measurements of photocatalytic activity and temperature is not controlled. In fact, phenomena related to the increase in temperature (for example evaporation) could be wrongly interpreted as photocatalytic degradation.

Pluronic F127 is a $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$ (PEO: polyethylene oxide, PPO: polypropylene oxide) triblock copolymer and has an average molecular weight of 13600 g mol^{-1} . PEO-PPO block copolymers have widespread industrial applications in detergency, emulsification, foaming, lubrication (16–18). More specialized applications are in pharmaceuticals, bioprocessing, and separation (19, 20). Block copolymers also show self-assembling properties and are commonly used in the synthesis of different ordered mesoporous materials (21–23). We have used Pluronic F127 as a sacri-

ficial organic material in place of stearic acid for photocatalysis experiments at temperatures higher than room temperature. A representative FTIR spectrum of Pluronic F127 is shown in the Supporting Information (Figure S3).

When Pluronic F127 was deposited on bare Si and heated at 25 and $100\text{ }^\circ\text{C}$, no significant change in the C–H band was detected, both with and without UV irradiation (Figure 3a, b). Similarly, when Pluronic F127 was deposited on TiO_2 and heated at $100\text{ }^\circ\text{C}$, but not exposed to UV light, no significant change in the integrated area of the C–H band was detected. These observations prove that neither direct interaction of the UV light with the copolymer nor thermal treatment cause significant evaporation or degradation of the block copolymer.

However, in block copolymer films deposited on the TiO_2 coatings and UV irradiated at $25\text{ }^\circ\text{C}$, a slight decrease in the C–H band intensity was detected, and after 60 min of UV irradiation, the concentration of organic species decreased 5% (Figure 2a). In the block copolymer films deposited on the TiO_2 coatings and UV irradiated at $100\text{ }^\circ\text{C}$, this decrease was dramatic: after 60 min an organic concentration drop of 95% was observed (Figure 3b). When the samples were heated at $150\text{ }^\circ\text{C}$, the organic content showed a marked decrease even if deposited on bare Si (Figure 3c).

A closer inspection of the FTIR spectra of the block copolymer deposited on TiO_2 films and UV irradiated at $100\text{ }^\circ\text{C}$ reveals the appearance of the C=O band centered at

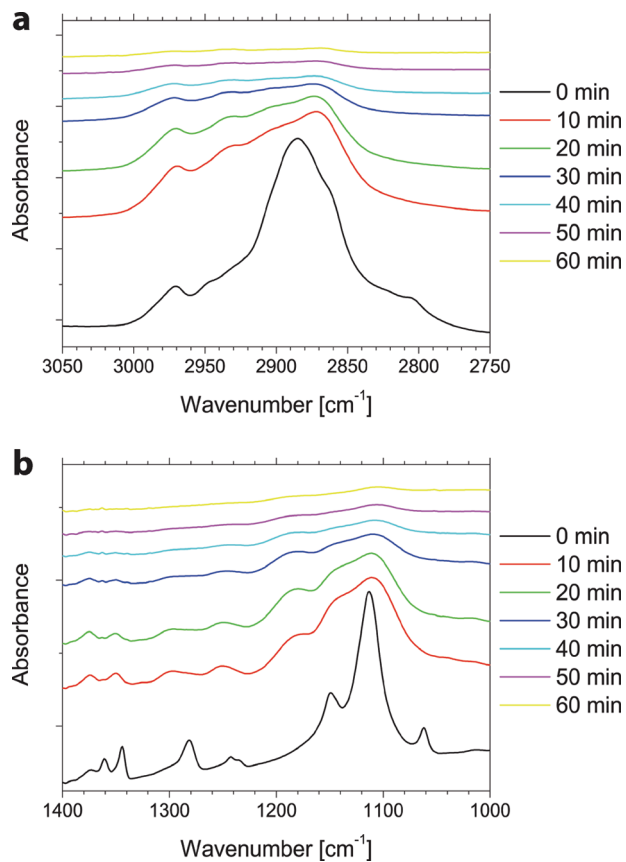


FIGURE 4. FTIR spectra of Pluronic F127 deposited on TiO₂ films and UV irradiated at 100 °C for different times. The (a) C–H and (b) C–O–C regions are shown.

1740 cm⁻¹ after 10 min irradiation (Figure 3d). Its intensity decreases at irradiation times greater than 20 min. This band originates from the carbonyl groups formed in the oxidation process of block copolymer and is typically observed as a byproduct of the decomposition reactions of the block copolymer (24, 25). Therefore, the presence of the carbonyl band can be explained by the formation of products from the degradation of Pluronic F127 by photocatalytic decomposition.

The appearance of the carbonyl band after 10 min of UV irradiation can be correlated with the increase in the O–H band centered at 3500 cm⁻¹ (not shown in figure). In the unexposed sample the weak signal at 3500 cm⁻¹ is mainly due to the OH groups at the ends of the copolymer backbones, whereas its increase after exposure is due to the products of the organic decomposition process. After 10 min UV exposure, the OH band increases, and then decreases again with longer exposure times.

The C–H absorption band in the range 3000–2800 cm⁻¹ (Figure 4a) is composed of two main contributions: one at higher wavenumbers, centered at 2970 cm⁻¹, which is associated to terminal CH₃ (methyl) groups (in polypropylene oxide or at the end of the polymeric backbone), and one at 2880 cm⁻¹, due to CH₂ (methylene) groups located in the middle of the copolymer backbone (17). The contribution at 2880 cm⁻¹ decreases sharply after 10 min exposure times, whereas the contribution at 2970 cm⁻¹ decreases more slowly with UV exposure time, because of the higher stability of methyl groups.

A more detailed study of the degradation process is beyond the scope of this letter and will be discussed more thoroughly in a future publication. However, it is important to observe that the decrease in the organic content at 100 °C is related mainly to photocatalytic activity (presence of C=O species) and does not consist of simple desorption of the block copolymer molecules, in which case the presence of carbonyl would not have been detected.

At 150 °C, the FTIR spectra of Pluronic F127 deposited on Si substrates show the formation of carbonyls after 10 min (see Figure S4 in the Supporting Information). This is consistent with thermal degradation and suggests that thermal cleavage of the copolymer backbone starts to occur around this temperature. However, thermogravimetric data found in the literature show that bulk Pluronic F127 samples are thermally stable up to ~250 °C (26). This difference can be explained considering that the present case deals with films, which are expected to have a different behavior than bulk samples (e.g., films have a larger exposed area). Moreover, the dependence of evaporation rate on molecular weight should be considered: the molecular weight of Pluronic F127 is much larger (~13 kDa) than that of stearic acid (284 Da), so the evaporation kinetics of stearic acid is expected to be faster. Therefore, it is reasonable to envision an interplay between different phenomena occurring at $T > 100$ °C in Pluronic F127 films, such as degradation, evaporation, and desorption of products from the surface.

Our data highlight that at moderate temperatures in the UV exposure of Pluronic F127 films deposited on TiO₂ surfaces, the predominant effect is largely determined by photocatalysis, which is remarkably enhanced by increasing the temperature. As a matter of fact, a 15-fold photocatalytic enhancement has been detected increasing the substrate temperature from room temperature to 100 °C.

CONCLUSIONS

TiO₂ represents an adaptive material that responds to the combined effect of UV irradiation and temperature. The photocatalytic activity of sol–gel TiO₂ films was measured using stearic acid and block copolymer Pluronic F127 as a function of UV irradiation time and substrate temperature. We found that between 50 and 75 °C, the process of stearic acid removal from the surface is strongly affected by evaporation, whereas Pluronic F127 is more stable and its removal from the substrate proceeds through photocatalytic oxidation of the macromolecule with production of intermediate oxidized products. This observation suggests that temperature should always be accurately controlled in the measurements of photocatalytic efficiency. We have also shown that block copolymer Pluronic F127 can be considered a possible choice for testing photocatalytic activity at moderate temperatures. Deposited on an inert substrate, Pluronic F127 is stable up to ~100 °C because it does not suffer from thermal degradation and evaporation, is stable under UV irradiation, and can be monitored by FTIR spectroscopy.

The enhancement of photocatalytic efficiency in TiO₂ coatings with temperature is a key point in building devices and setting up characterization and validation protocols.

Household appliances, air and water purification, and sterilization devices for medical applications are only a few of the possible applications taking advantage of the superior photocatalytic properties induced by the UV-thermal combined effect.

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Supporting Information Available: Experimental procedure for the synthesis of the TiO₂ films, FTIR spectrum of Pluronic F127, XRD pattern of a TiO₂ film, additional FTIR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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