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Photocatalytic thin films coupled with polymeric microcapsules for the controlled-release of volatile agents upon solar activation

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Abstract. This work reports on the application of solar-activated photocatalytic thin films that allow the controlled-release of volatile agents (e.g., insecticides, repellents) from the interior of adsorbed polymeric microcapsules. In order to standardize the tests, a quantification of the inherent controlled-release of a particular volatile agent is determined by gas chromatography coupled to mass spectroscopy, so that an application can be offered to a wide range of supports from various industrial sectors, such as in textiles (clothing, curtains, mosquito nets). This technology takes advantage of the established photocatalytic property of titanium dioxide (TiO₂) for the use as an active surface/site to promote the controlled-release of a specific vapor (volatile agent) from within the aforementioned microcapsules.

1. Introduction

The microencapsulation for the controlled-release of dispersive agents appeared very recently with applications in various areas [1-3]. In one case the authors report an application with emphasis in killing or repelling insects from solar activated materials [4]. In this particular case, this nanotechnology refers to the controlled-release of vapors from within polymeric microcapsules mediated by mechanisms of photocatalysis. Titanium dioxide (TiO₂) is a semiconductor material increasingly reported as photoactive due to the intrinsic photocatalytic ability to dissociate organic pollutants adsorbed on its surface upon direct action of solar light [5-7]. Hence, these oxidation-reduction mechanisms can be triggered to dissociate and break-down the polymeric structure of capsules and thus yield a controlled-release of volatile agents (e.g., insecticides, repellents, deodorants, fragrances, etc.). In the case of insecticides and repellents, this technology should be very promising for the prevention of diseases transmitted by airborne insect carriers, such as dengue and malaria; in particular for remote areas in third-world countries without access to electrical supply. The photocatalytic material can be either in the form of a nanostructured thin film or nanoparticles, depending on the final support where they will be coated onto. In Figure 1 it is illustrated the layers of the heterostructured material, comprising: a chosen substrate (1) that can be of several types, such as glass, plastic, ceramic, metal, stone, wood, textile, amongst others; a photocatalytic thin film (2) where subsequently the volatile agent-containing microcapsules (3) can be adsorbed onto.



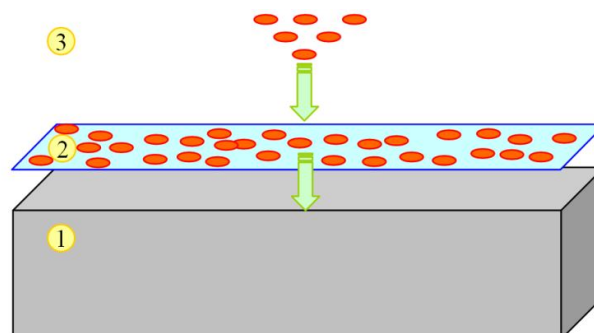


Figure 1. Layers representing the heterostructured material: substrate (1); photocatalytic thin film (2); volatile agent-containing microcapsules (3).

This research focuses on the production of a functional heterostructured material, which may be deposited or attached to various types of surfaces (glass panels, tiles, lamps, textile nets and clothes) in order to induce the controlled-release of a volatile agent. For the particular case of an insecticide or repellent, during daylight the volatile agent is gradually released, being the controlled-release output proportional to the solar radiation projected onto the surface of the photocatalyst-microcapsule system [4]. The solar-activated material has been produced in the form of thin films by reactive sputtering deposition on glass substrates. Several inherent experimental parameters allow the optimization of the resulting thin films. In this work, a specific focus is given to the sputtering gas flow rate. Other experimental parameters such as target power density have been published elsewhere [8,9]. Furthermore, the microcapsule synthesis, volatile agent encapsulation and controlled-release monitoring procedures are also described. Dodecane was selected as a test volatile agent and polyamide/poly(vinyl alcohol) for the formation of the microcapsule. Its output release has been monitored by gas chromatography coupled with mass spectroscopy (GC-MS).

2. Materials and methods

2.1 Materials

All reagents used for preparation of volatile agent and polymeric microcapsules were supplied by Sigma-Aldrich. Deionized water served as the solvent. The microcapsules were synthesized by poly(vinyl alcohol) (PVA – $(C_2H_4O)_x$), ethylenediamine ($C_2H_8N_2$) and sebacoyl chloride ($C_{10}H_{16}Cl_2O_2$) which determines the wall thickness [10], with dodecane ($C_{12}H_{26}$) as encapsulated volatile agent.

2.2 Methods

2.2.1 Synthesis of the TiO_2 thin films

The titanium dioxide thin films were synthesized by physical vapor deposition (PVD). In reactive magnetron sputtering mode, impinging argon ions eject titanium atoms from a high purity Ti target, which are subsequently bonded to reactive oxygen molecules when condensing in the glass substrate. Prior to deposition, a base pressure of the order of 10^{-4} Pa was attained in the vacuum chamber. The flow of the oxygen reactive gas was kept constant at 8 sccm for all depositions, while the argon flow rate (working gas) was varied between 35 and 275 sccm. A small amount of nitrogen (<30% of total reactive gas) was also introduced in order to dope the TiO_2 lattice with substitutional N anions, which has been proven to reduce the semiconductor band-gap (3.2 eV) and hence enhance the absorption of visible light beyond this absorption threshold [11]. The level of anionic N-doping in the titanium dioxide lattice has been determined elsewhere [12], and is of the order of ~1.2 at. %. The as-deposited coatings are mostly amorphous; in order to induce crystallinity, these coatings were post-annealed in a

high-vacuum furnace, at 500 °C. With this procedure, an improvement of the optical and photocatalytic properties of the thin films was achieved. The average film thickness is ~500 nm.

2.2.2 Synthesis of the formation process of capsules and encapsulation

Polyamide/PVA was chosen for the polymeric microcapsule material that encloses the volatile agent. Under ultrasonic conditions, 265 μL of ethylenediamine was added to the 25 mL of PVA aqueous solution (2%), followed by the addition, drop-by-drop, of a solution of sebacoyl chloride (215 μL) in 2.5 mL of dodecane (the volatile agent). Finally, the emulsion was kept for 5 minutes under ultrasonic agitation and an additional 5 minutes under magnetic stirring. The excess of solvent was removed by washing the microcapsules with deionized water. Sebacoyl chloride and ethylenediamine are essential for the encapsulation of dodecane into the microcapsules as an interfacial polymerization process occurs at the water/dodecane interface leading to a polyamide/PVA polymer film that encloses the organic phase. The resulting microcapsules have a liquid doughy aspect. As the physical state of the dodecane-loaded microcapsules is distinct from that of the photocatalytic thin films, it is possible to carry out their bonding by simple physical adsorption without using any chemical reaction; thus, a dispersion of microcapsules was adsorbed onto the photocatalytic thin film samples.

3. Results and discussion

3.1 Evaluation of the photocatalytic activity of the TiO_2 thin films

The assessment of the photocatalytic activity is essential to characterize the efficiency of the TiO_2 thin films. For such, the thin films were immersed in an aqueous solution of a dye, methylene blue (MB), acting as an organic pollutant simulator, and subjected to ultraviolet (UV) irradiation for six hours, with an excitation broad-band centered at 380 nm (UV-A). After measuring the dye's absorbance decay with irradiation time (t), and considering its initial concentration ($C_0=10^{-5}$ M), it was then possible to determine the first-order kinetic degradation rate constant, k , from $\ln(C/C_0)=-kt$, where C represents the dye's concentration, which is proportional to its optical absorbance.

A correlation of the sputtering working gas (argon) flow rate during deposition with k is illustrated in Figure 2. It was noticed that an increase in argon flow rate up to 250 sccm enhanced the dye degradation efficiency of thin films to a maximum value of $5.3 \times 10^{-3} \text{ min}^{-1}$; above 250 sccm this degradation rate was slightly reduced ($5.1 \times 10^{-3} \text{ min}^{-1}$). It should be noted that for the $\text{TiO}_2\text{:N}$ films deposited with higher Ar flow rates during sputtering, 250 and 275 sccm, the $\ln(C/C_0)$ evolution with time is biphasic; the k values for these two samples that are presented in Figure 2 are ascribed to the first hour of the experiment; the corresponding values for the subsequent assay are $2.1 \times 10^{-3} \text{ min}^{-1}$ and $1.2 \times 10^{-3} \text{ min}^{-1}$, respectively. For optimized conditions, after 6 hours of UV-A irradiation with a relatively low irradiance of $\sim 2 \text{ mW/cm}^2$, the main absorbance peak of the MB dye, and thus its concentration, decreased more than 60%. The variation in k between the minimum and maximum value is approximately one order of magnitude.

Another method to test the photocatalytic effect is to observe the hydrophilicity nature of the surface upon light exposure. In figure 3 it can be seen the evolution of the water contact angle of a 20 μL water droplet on the surface of three TiO_2 thin films, deposited with varying sputtering Ar flow (in sccm), as a function of irradiation time. The data corroborates with the former data presented in figure 2; as the working gas flow rate increases up to 250 sccm the water contact angle is decreased from $\sim 70^\circ$ to $\sim 20^\circ$; above 250 sccm the water contact angle increases to $>40^\circ$ (not shown). For the hydrophilicity experiments, the samples were pre-irradiated for determined period of time with a 150 W Xe arc lamp, using its full spectrum and with an irradiance level of $\sim 10 \text{ mW/cm}^2$; the contact angle measurements were averaged from 3 droplets per sample at the specified time interval.

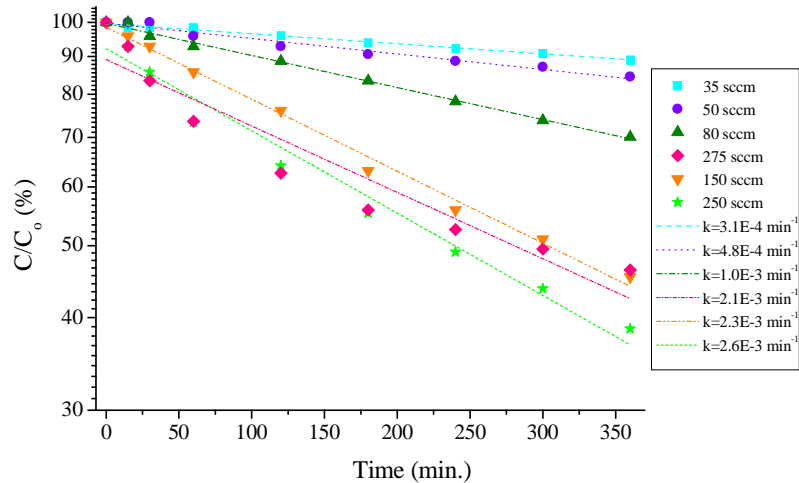


Figure 2. Variation of the 1st-order dye degradation rate as a function of working gas (Ar) flow during the sputtering process.

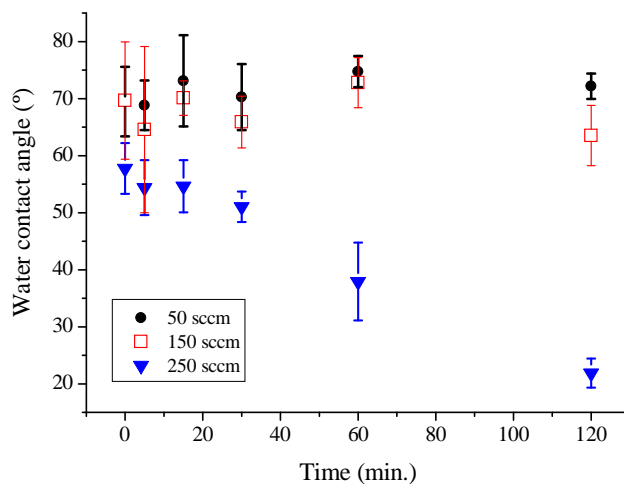


Figure 3. Variation of the water contact angle as a function of working gas (Ar) flow during the sputtering process.

X-ray diffraction (XRD) is essential for the crystallographic analysis of the thin films, allowing, in this particular case, the identification of anatase and rutile as the active crystalline phases of TiO_2 , as it can be seen in the diffractograms presented in Figure 4, where A and R stand for anatase and rutile, respectively. For lower argon flow rates, and thus lower thin film deposition rates, both anatase and rutile phases are discerned, being the latter diminished for higher Ar flow rates. The average crystallite domain size is ~ 30 nm. This trend is compatible with the photo degradation results, as anatase is known to be much more active than rutile.

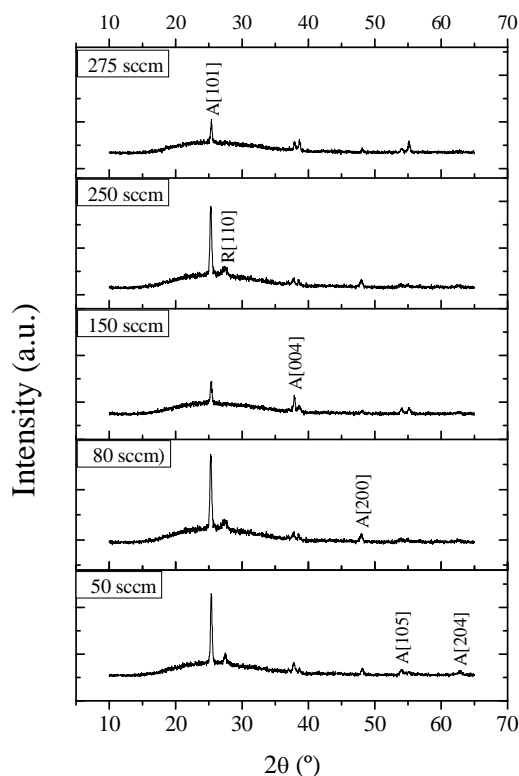


Figure 4. X-ray diffraction patterns for TiO₂ films produced by PVD under varying sputtering gas (Ar) conditions.

3.2 Evaluation the controlled-release by (GC-MS)

The main objective of this study is to upon ultraviolet irradiation evaluate the photocatalysis-induced dissociation process of polymeric microcapsule wall, and subsequent volatile agent release yield, in the presence of TiO₂ thin films. The UV-light driven redox mechanisms are responsible for the microcapsule structure rupture with subsequent release of the volatile agent. For this purpose, gas chromatography coupled to mass spectroscopy allows, besides accurate indexing, the quantification of the released compounds. Different experiments were performed: in the presence and absence of TiO₂ thin films, each with and without UV-A irradiation (6.7 mW/cm², centered at 365 nm) for two hours. A polydimethylsiloxane (PDMS) fiber was placed in a vial headspace for 20 minutes, for the adsorption of the released volatile compounds, and then it was proceeded with GC-MS analysis. The experiment was repeated in the absence of UV-A radiation and results were compared in order to verify the difference in intensity.

The GC-MS analysis of the UV-A irradiated samples containing dodecane-loaded microcapsules adsorbed onto TiO₂ thin films revealed the presence of dodecane as the principal volatile compound which was released. The chromatograph obtained for the pre-irradiated dodecane-loaded polyamide/PVA microcapsules in the presence and absence of a TiO₂ thin film is given in Figure 4a), while in Figure 4b) a comparison between with and without UV-A irradiation is shown. The chromatographs reveal the peak of dodecane for different experiments. Comparing the UV-A pre-irradiated sample with and without TiO₂ (Figure 4a) it is evident that the area of the dodecane peak is much higher when the dodecane-loaded microcapsules are adsorbed onto the photocatalytic thin film. As it can be seen from both Figures 5a) and b), even without TiO₂ nor UV-A pre-irradiation, some dodecane is released, since the microcapsule hermetical property is still not perfect; this work is in progress and this deficiency has to be attenuated.

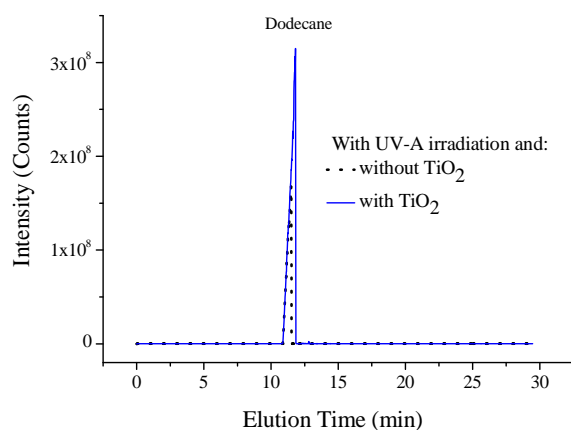


Figure 5a). Chromatograph obtained by GC-MS for dodecane-loaded polyamide/PVA with and without layering onto a TiO₂ thin film, after UV-A irradiation.

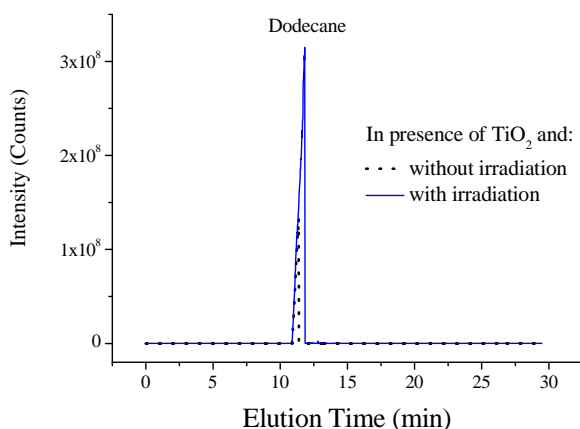


Figure 5b). Chromatograph obtained by GC-MS for dodecane-loaded polyamide/PVA microcapsules that were layered onto a TiO₂ thin film, with and without previous UV-A irradiation.

Figure 6. shows the output concentrations (in ppm) of dodecane obtained from the microcapsules, for different samples and experimental conditions. It can be seen that for this particular case and volatile agent formulation, the maximum output concentration of dodecane was of the order of 160 ppm.

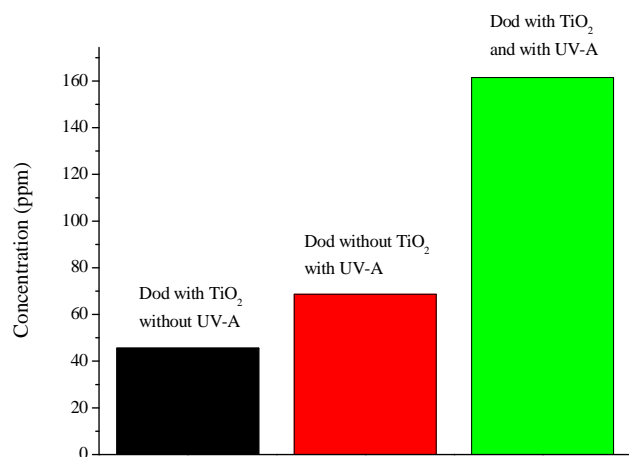


Figure 6. Output release of dodecane (Dod) from the polyamide/PVA microcapsules with and without the presence of the photocatalyst TiO₂ thin film and with and without previous UV-A illumination experiments.

Figure 7. shows a scanning electron microscopy (SEM) micrograph of the dodecane-loaded polyamide/PVA microcapsules, with diameters ranging from 70-100 μm . The spherical nature of these capsules and the porous structure of the outer walls can be observed from this figure.

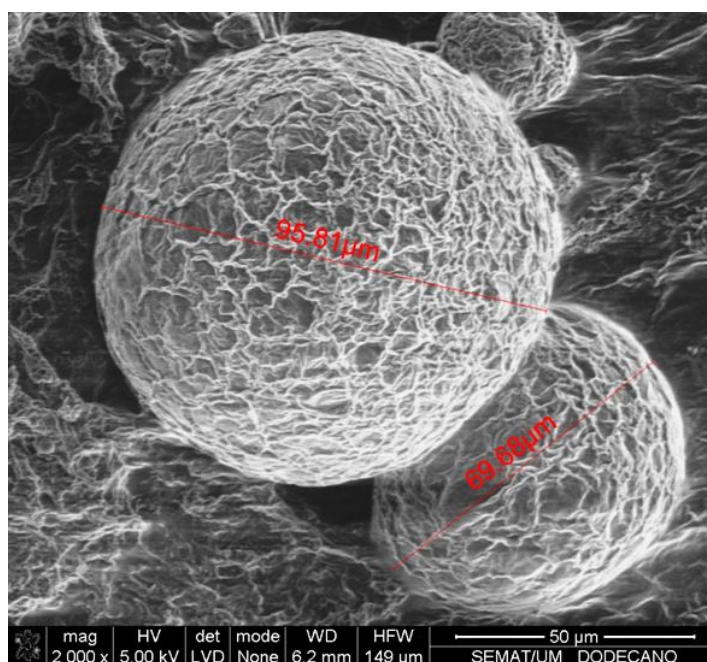


Figure 7. SEM micrograph of dodecane-loaded polyamide/PVA microcapsules

4. Conclusion

The results shown in this work permit to conclude that the overall photocatalytic performance of the TiO₂ thin films can be improved by tailoring specific process parameters, such as the sputtering working gas flow rate; as it was increased from 35 to 250 sccm, the efficiency in degrading a chosen organic dye and the hydrophilic nature of the surface were improved; however, above the latter value the efficiency was reduced. Furthermore, for higher Ar flow rates the rutile formation is inhibited, leaving anatase as the prominent photocatalytic active polymorph with an average crystallite size of ~30 nm. It was possible to demonstrate by means of GC-MS experiments that for optimized conditions upon UV-

A irradiation of dodecane-loaded polyamide/PVA microcapsules this compound was, in fact, released, identified and quantified. Nevertheless, further work must be endured to improve the polymeric microcapsule synthesis, in order to become more hermetical. Therefore, evidence is provided for the controlled-release of a chosen volatile agent by light activation of a thin film surface.

Acknowledgments

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