

Ag-MODIFIED VANADIUM OXIDE PHOTOCATALYTIC THIN FILMS DEPOSITED BY A TWO PARALLEL ABLATION PLASMAS CONFIGURATION

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The application of a two ablation plasmas configuration to deposit vanadium oxide thin films modified with different amounts of silver is reported. In this configuration, two parallel plasmas are produced ablating simultaneously two different targets, V and Ag, to form the Ag-modified vanadium oxide thin films. The ablation of the vanadium target is performed under constant conditions in all deposits, while the silver produced plasma is varied. The effect of the amount of Ag incorporated in the films on their compositional, morphological, structural, and photocatalytic properties is studied. The results reveal that films with variable Ag content from 0.6 to 17.2 at. % are obtained. Depending on the silver content, the samples show very different surface morphologies from smooth surfaces to acicular structures in films containing Ag. Raman spectra reveal that as the silver content is increased different vanadium oxides coexist and at the highest Ag content a silver vanadate is formed. The photocatalytic activity for the degradation of the Malachite Green dye under simulated solar light is determined. It is found that in general terms, films containing silver show a higher photocatalytic response than V₂O₅ films alone.

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1. Introduction

In recent years, wastewaters from both domestic and industrial uses have created a major environmental problem because these are in many cases released into the soil and aquifers with the consequent pollution of water. Among the pollutants in wastewaters are organic compounds such as phenols, dyes, pesticides, drugs, solvents and fertilizers. Most of these compounds are toxic to humans and other living organisms, even when they are present in low concentrations [1]. Among the most extended methods for the removal of organic compounds in water are the Advanced Oxidation Technologies (AOTs). These methods are based on effective physicochemical processes that produce important changes in the chemical structure of organic compounds including their complete mineralization (transformation of organic compounds to CO₂ and water). V₂O₅ is an interesting alternative material to be used for photocatalytic applications, because of its low band gap (2.8 eV) can be photoactive under visible irradiation as shown some years ago [2]. Additionally, due to its different oxidation states, from V²⁺ a V⁵⁺, vanadium can form a broad variety of oxides such as V₆O₁₃, VO₂, V₈O₁₅, V₇O₁₃, V₆O₁₁, and V₂O₃, among others [3]. Several strategies have been proposed to improve the photocatalytic activity of some semiconductors, these include doping with metals and non-metals, coupling of semiconductors and sensitization with organic dyes [4]. Particularly, coupling of semiconductors has been considered as a good alternative to develop high efficiency photocatalyst materials that can compensate the

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disadvantages of the individual components inducing synergistic effects such as efficient charge separation, band gap narrowing and consequently improvement of their photocatalytic performance. However, much work is still necessary to vary the composition in a controlled way and therefore, a lot of work has been devoted in the last years to investigate deposition techniques capable to prepare oxide thin films modified with metals by controlling the amount of these. In this line, our research group has been working in the implementation of different variants of the laser ablation technique to improve some properties of the deposits and even to obtain new materials. The preparation of thin films applying alternative configurations of laser ablation have been successfully used to prepare TiAlN [5], Co:TiO₂ [6], and V₂O₅:Ag [7] thin films with good control of the composition. In particular, the use of two different plasmas has several advantages since it allows: a) to control the composition of the deposited films by varying the plasma parameters of one of them; b) if the plasmas are produced sequentially, multilayer structures can be fabricated easily; c) thin films with embedded nanoparticles can be prepared directly. In this work, the preparation of vanadium oxide thin films with different amounts of silver using a two parallel ablation plasmas configuration is reported, and their photo-catalytic performance is also evaluated. It must be pointed out that with this configuration we have extended the range of silver loads reported in a previous paper [7], in which a hybrid configuration was employed, obtaining different materials and even improving the photocatalytic activity.

2. Experimental procedure

2.1 Thin film preparation

Thin films were deposited by the combination of two laser ablation plasmas propagating in parallel directions. The plasma plumes were produced by laser ablation using a Nd:YAG laser with emission at the fundamental line (1064 nm) with 10 ns pulse duration; the laser beam was divided in two using a beam splitter. The laser beams were focused onto the targets with 50-cm focal length spherical lenses. High purity (99.99%) vanadium and silver targets were used as material sources. The laser fluence on the V target was constant close to 8.2 J/cm². By varying the laser fluence on the silver target, from 0.2 to 1.8 J/cm², the effect of the Ag plasma parameters on the physical properties of the deposited vanadium oxide thin films modified with different amounts of silver was investigated. Therefore, during the experiments, the vanadium and the silver plasmas combine at the substrate resulting in an Ag:V₂O₅ film. The target to substrate distance was set at 5 cm and the deposition time was 60 min. Thin films were deposited at room temperature onto glass substrates (1x1 inch) and pieces of Si (111).

2.2 Plasma characterization

Determination of the plasma parameters, i.e., the average kinetic energy of ions and the plasma density, was performed by the Time of Flight analysis (TOF) from measurements carried out using a Langmuir planar probe (6 mm diameter). In all the experiments the probe was biased at -40 V, where the ion current is saturated, monitoring the voltage through a 15 Ω resistor. The plasma density was determined from the maximum ion current across the resistor. Measurements were performed under the experimental conditions used for thin film deposition in an attempt to establish a correlation between plasma parameters and thin film properties.

2.3 Thin film characterization

The silver content incorporated in the films, as well as the bonding features of the elements present, were determined by X-ray Photoelectron Spectroscopy (XPS); measurements were done using a K-Alpha Thermo Scientific XPS. Vibrational features of deposited films were characterized by Raman spectroscopy; the Raman spectra were acquired using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope; a Nd:YAG laser beam (532 nm) was focused with a 100 X objective onto the sample surface. The effect of the Ag content on the surface morphology of the films was observed by Scanning Electron Microscopy (SEM) using a JEOL JSM 6510LV microscope. The photocatalytic performance of the Ag:V₂O₅ thin films was evaluated through the degradation of a 10 μmol/l solution of malachite green (MG) dye

(C₂₃H₂₅ClN₂); the catalysts were activated by illumination with a solar simulator using a power density of 30 mW/cm² setting the light source at a height of 40 cm from the solution surface; dye degradation was monitored by the decrease in the characteristic absorption band of the MG peaking at 619 nm, taking aliquots every 15 minutes during the reaction process.

3. Results and discussion

3.1 Plasmas characterization

The Langmuir probe measurements were performed for the individual plasmas as well as for the combined plasmas. The mean V and Ag ion kinetic energies were determined from the TOF probe curves. The calculations were carried out assuming that the ions incident on the probe were predominantly V and Ag ionized once. The plasma densities were calculated from the maximum values of current collected by the probe. The results showed that the vanadium plasma parameters used for deposition were a mean V⁺ kinetic energy (E_V) of 114 eV with a plasma density (D_p) of 4.7 × 10¹² cm⁻³. As it was mentioned in the thin film preparation section, the laser fluence on the silver target was varied in order to study the effect of the silver plasma parameters on the properties of the Ag:V₂O₅ films. Fig. 1a shows a typical set of time of flight curves obtained from the Langmuir-probe measurements of the Ag plasmas produced at different laser fluences. It can be observed that as the laser fluence decreases the maximum in the TOF curve is shifted to longer times and at the same time the intensity decreases strongly. This behavior is indicative of a reduction of the ion kinetic energy and the plasma density. Fig. 1b shows the mean ion kinetic energy and plasma density plot, it is clearly seen that the mean Ag⁺ kinetic energy varied from 50.0 up to 224.0 eV, and the plasma density from 1.1 × 10¹¹ up to 3.9 × 10¹² cm⁻³. These were the plasma conditions under which deposition of films was carried out.

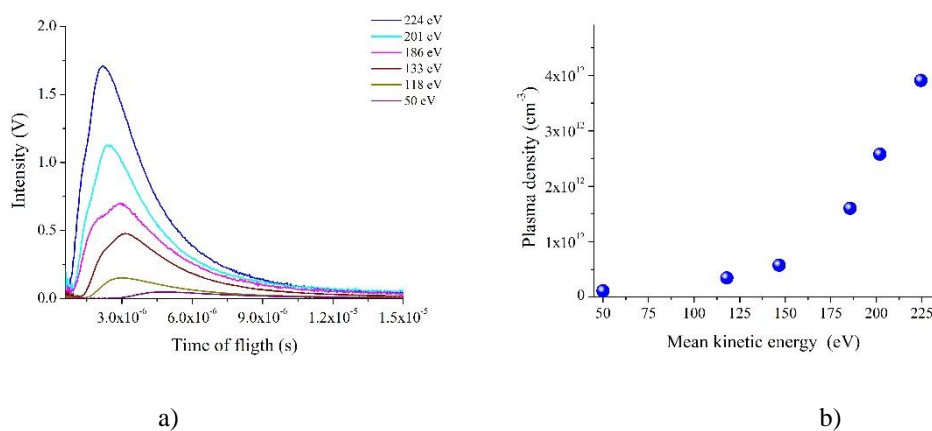


Fig. 1. a) Typical time of flight (TOF) curves obtained from the Langmuir-probe measurements of the Ag plasmas produced at different laser fluences; b) The plasma density and ion energy plot indicating the plasma conditions under which deposition of films was carried out.

3.2 Compositional characterization

The XPS results show that the deposited films have Ag contents from 1.7 to 17.2 at.% depending on the Ag plasma conditions used for thin-film deposition. In Fig. 2a and 2b the Ag atomic concentration for the films as a function of the ion energy and plasma density are presented. It can be clearly observed that the atomic concentration of silver as a function of the Ag⁺ kinetic energy follows an approximately linear behavior for energies greater than 118 eV. A different behavior as a function of the plasma density is observed, however, in general terms, the Ag content increases as the plasma parameters increase. According to Fig. 2b, the higher the kinetic energy the higher the plasma density, which implies that more Ag species are available for

incorporation in the film. It is worth noting that the results in fig. 2b suggest that at higher plasma densities the Ag incorporation rate seems to decrease.

The high-resolution XPS spectra corresponding to the V2p region are shown in figure 2c. The spectrum of the film without silver, shows a doublet at 517.1 and 524.6 eV attributed to the 2p_{3/2} and 2p_{1/2} V⁵⁺ levels of V₂O₅ [8]. When Ag is incorporated into the film, additionally to the signals at 517.1 and 524.6 eV, the spectra show shoulders peaking at 515.5 and 523.5 eV that are assigned to V⁴⁺ indicating the presence of VO₂ [9]. At 17.2 at. % of Ag the signals appear at 517.1 and 524.6 eV and become broader suggesting a lower oxidation state of V which can be assigned to AgVO₃ [10].

Fig. 2d shows the high-resolution XPS spectra for the Ag3d region. Two peaks around 368 and 374 eV attributed to the 3d_{5/2} and 3d_{3/2} levels respectively are present; the spectrum of high purity silver is included for comparison purposes. The spectra of the films with silver contents of 6.2, 8.1 and 17.2, at. % show peaks at 367.4 and 373.4 eV attributed to Ag⁺ [11]. Further increase in Ag content shifts the peaks towards 367.9 and 374.1 eV suggesting the co-existence of Ag⁰ and Ag⁺. At the highest Ag content, the peaks are located at 368.2 and 374.3 eV revealing the presence of metallic silver (Ag⁰) [11] in the prepared compounds. This last result could be attributed to the formation of silver quasi-spherical particles with sizes in the microscale due to coalescence processes as more Ag is incorporated into de films as it will be shown in the morphological characterization results.

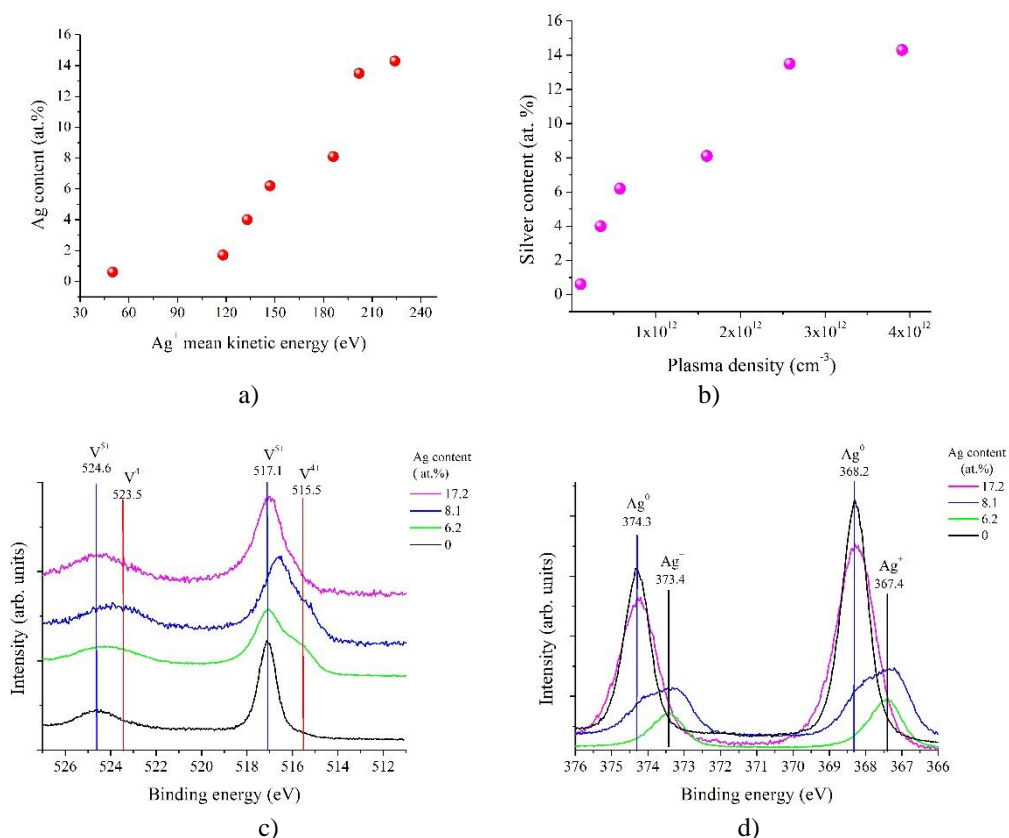


Fig. 2. Ag content as a function of: a) the Ag⁺ mean ion kinetic energy; b) the plasma density; c) high-resolution XPS spectra for the V2p region for different samples; d) high-resolution XPS spectra for the Ag3d region for different samples.

3.3 Raman characterization

In Fig. 3 the Raman spectra of the different samples deposited on Si are shown. The Raman spectrum corresponding to the thin film without silver, consists of peaks at 145, 197, 284, 305, 407, 482, 702 y 996 cm⁻¹, accordingly to those reported for crystalline V₂O₅ [12]. The peak at

994 cm^{-1} is assigned to the stretching mode related to the Ag symmetric mode of the short vanadium oxygen (V=O) bond. The peak at 765 cm^{-1} is assigned to the bending of the V-O-V bond. The peak at 702 cm^{-1} is characteristic of the stretching mode of the V_3O bond. Finally, the peak with highest intensity pointing at 145 cm^{-1} attributed to the bending mode of the skeleton while the bands around 300 cm^{-1} are due to bending modes of VO_3 groups [12]. The Raman spectra of the samples with 1.7 at.% of silver are very similar to the sample without silver, showing the same peaks but with lower intensity. The Raman spectra of the samples with an Ag content of 8.1 and 14.3 at.% show additional peaks at 222, 256, 267, 313, 381, and 440 cm^{-1} attributed to VO_2 [13]; furthermore Raman signals are observed at 128, 312 and 697 cm^{-1} which are attributed specifically to V_6O_{13} [14]. In addition, the Raman spectra of the samples with 8.1 and 14.3 at.% of Ag, show features at 163, 894 and 940 cm^{-1} that could be assigned to vanadium oxide nanotubes (VOx NT) [15]. The peak at 766 cm^{-1} remains unidentified. At the highest Ag content, the corresponding Raman spectrum show peaks at 172, 249, 338, 388, 699, 734, 808, 846 and 885 cm^{-1} attributed unambiguously to the AgVO_3 silver vanadate [16]. Therefore, according to the Raman results the structural evolution of the crystalline phases, as the silver content increases, is the following: the starting material consist of V_2O_5 , when silver is incorporated in low concentrations the crystalline structure remains but slightly distorted due to the Ag incorporation into the V_2O_5 lattice; as the silver content increases the structure changes radically to VO_2 coexisting with V_6O_{13} and VOx NT; the subsequent increase in silver leads finally to films only of AgVO_3 . Table 1 resumes the crystalline evolution of the prepared Ag-modified vanadium oxide thin films as a function of the Ag content.

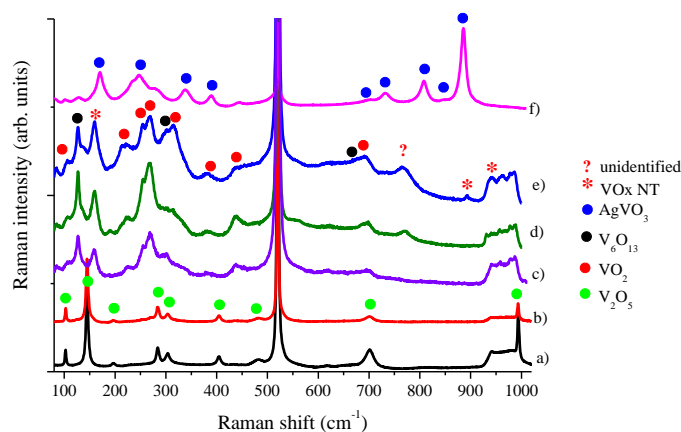


Fig. 3. Raman spectra of samples deposited on Si with different silver content: a) V_2O_5 without Ag, b) Ag = 6.2 at.%, c) Ag = 8.1 at.%, d) Ag = 14.3 at.%, and e) Ag = 17.2 at.%. f) AgVO_3 .

Table 1. Crystalline evolution of films as a function of Ag content.

Ag content (at. %)	0	1.7	6.2-8.1	14.3	17.2
Crystalline phases present	V_2O_5	V_2O_5	$\text{VO}_2 + \text{V}_6\text{O}_{13}$ +VOx NT	$\text{VO}_2 + \text{V}_6\text{O}_{13}$ +VOx NT	AgVO_3

3.4 Morphological characterization

The SEM images of films with different Ag content are shown in figure 4. The samples without Ag and with 1.7 at. % of Ag show very smooth surfaces as is observed in figure 4a for the sample with 1.7% of Ag. As low amounts of silver are incorporated in the film, the surface becomes nanostructured as is clearly observed in figure 4b; the sample's surface with an Ag content of 8.1 at. % is covered with some acicular shape structures, with lengths about 12 μm and widths close to 500 nm, as is shown in figure 4c. The size of these nanostructures increases when

increasing the amount of silver in the film to 14.3 at.%, reaching widths close to 1-2 μm while their length increase until 30-20 μm . Finally, at the highest Ag content, 17.2 at. %, the surface is covered by nanostructures with sizes close to 1 and 40 μm of width and length respectively. In addition, the presence of quasi-spherical particles with average diameters of 3.5 μm is observed.

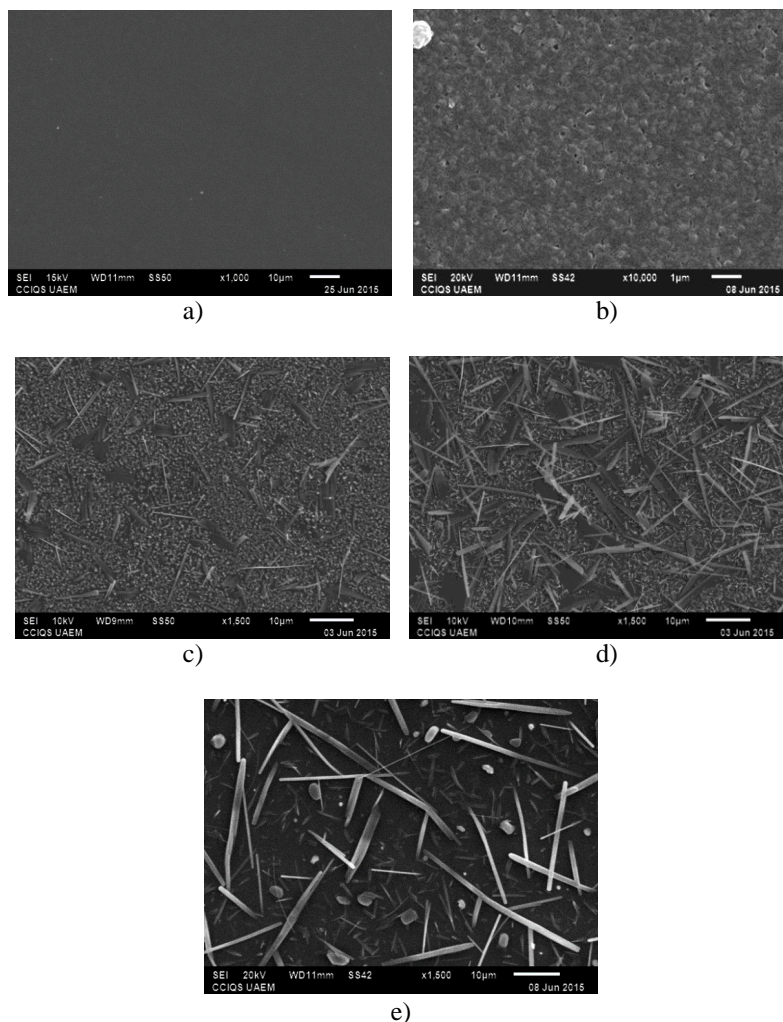


Fig. 4. SEM images of films with different Ag content: a) V_2O_5 without Ag, b) Ag = 6.2 at. %, c) Ag = 8.1 at. %, d) Ag = 14.3 at. %, and e) Ag = 17.2 at. %.

3.5 Photocatalytic performance

The malachite green dye degradation was monitored through the decrease of its characteristic absorption band peaking at 619 nm. It is worth mentioning that additional peaks were not observed in the UV-Vis spectra, suggesting the absence of intermediary's organic compounds; in fact, some Total Organic Carbon (TOC) measurements suggest that the preferred reaction route is mineralization, that is, the transformation of the organic molecule to CO_2 and water. Fig. 5a shows the degree of degradation as a function of the reaction time under irradiation with a solar simulator at a power density close to $30 \text{ mW}/\text{cm}^2$. It is observed that the unmodified V_2O_5 film reach a degradation degree of 27% after 210 min of reaction; the addition of low contents of Ag, results in a photocatalytic response of 36%, better than the response of the V_2O_5 film in approximately 33%. The film containing 6.2 at.% of silver exhibit the best photocatalytic response, reaching conversions close to 63%, almost 130% greater than the conversion achieved by the V_2O_5 film alone. Further addition of Ag to 8.1 at. % decreases the degradation degree close to the observed for the film with a silver content of 1.7 at.%. The film with the highest Ag content,

17.2 at. % shows an increase to 35% of conversion. Fig. 5b shows the degradation degree at a reaction time of 120 min, in which it is clearly observed that a silver content of 6.2 at. % provides the highest conversion.

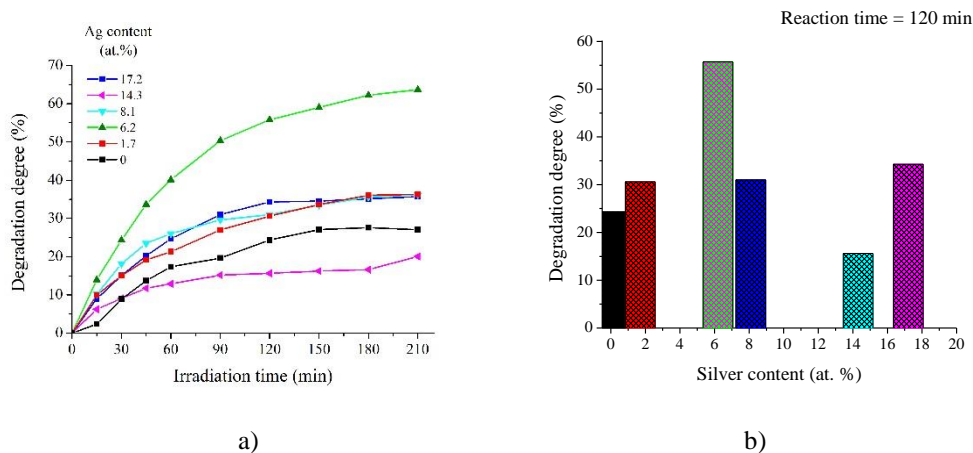


Fig. 5. a) Degree of degradation as a function of the reaction time under irradiation with simulated solar light; b) degradation degree at a reaction time of 120 min for the samples with different Ag contents.

4. Conclusions

A two parallel ablation plasmas deposition configuration in which the film is formed by the interaction of two different plasmas was successfully employed to prepare vanadium oxide thin films modified with different contents of silver. The incorporation of Ag in the films has important effects on the properties of the obtained materials. The structural characterization reveals that silver incorporation promotes a crystalline evolution from V_2O_5 to mixtures of VO_2 coexisting with V_6O_{13} and VO_x NT and finally of $AgVO_3$. The surface morphology is also strongly affected by the Ag content changing from a very smooth surface to nanostructured surfaces resulting in morphologies that could be useful for photocatalysis since the effective surface area is controlled. In general terms, the films containing silver exhibit better photocatalytic performances for the MG dye degradation than the unmodified V_2O_5 films, reaching a degradation degree for the 6.2 Ag content 130% higher than the one achieved by the V_2O_5 film alone.

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