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Thin films of titanium dioxide modified with MoO₃ nanostructures for photocatalytic applications

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Abstract. TiO₂ thin films modified with MoO₃ nanostructures were obtained by the spin coating technique. The precursors solutions were prepared by the sol-gel technique adding colloids of Mo-based nanostructures prepared by laser irradiation of powders suspended in liquid media. It was found that MoO₃ layered nanostructures form the prepared colloidal solutions. The obtained films were characterized by X-Ray Photoelectron, Raman, Ultraviolet-Visible and PL Spectroscopies, and Scanning Electron Microscopy. XPS reveal the presence of TiO₂ and MoO₃ in the films. Raman results show that crystalline TiO₂ in its anatase phase is obtained. These results indicate that the films are forming composites in which nanostructures of molybdenum trioxide are incorporated in the titania film. Optical measurements show that the band gap energy for all samples vary from 3.3 to 3.5 eV.

1. Introduction

In recent decades, photocatalysis has been extensively investigated due to its potential applications for the treatment of polluted water with organic molecules. In general terms, photocatalysis is based on the reactions that occur on the surface of a semiconductor under UV light irradiation resulting in the generation of oxidizing agents and reducing radicals that can decompose any type of organic matter into carbon dioxide and water, a process called mineralization [1]. Among the most important advantages of photocatalysis it can be mentioned the possibility of reusing the material making this process cheap as well as the option of using solar light as energy source. Titanium dioxide (TiO₂) is a semiconductor with a bang gap around 3.0 eV and has been considered the ideal photocatalyst due to its physicochemical properties such as, no-soluble in liquid medium, cheap, can be reused, it has high resistance to photochemical corrosion and allows to carry out the photocatalytic process at room temperature [2]. It is important to mention that titania is photoactive only under UV irradiation being its major disadvantage because the use of UV radiation involves its generation, for example, by mercury vapor discharge lamps, which consumes electrical energy. Another disadvantage is that the recombination of photogenerated electron-holes pairs occurs in very short times, of the order of nanoseconds, which is traduced in a very low efficiency [3]. Therefore, in recent years many efforts have been devoted to developing photocatalysts based on TiO₂ capable of absorbing wavelengths in the visible region to take advantage of the solar radiation as well as to reduce the recombination rate of



the electron-hole pairs. Among the strategies proposed to improve the photocatalytic activity of titania, the doping with metals and nonmetals as well as the coupling of semiconductors forming heterostructures [4], have been considered good alternatives to induce the band gap narrowing as well as to promote the separation of the photo-induced charge carriers decreasing the electron-hole recombination processes. Therefore, becomes particularly important to investigate thin film deposition alternatives to growth nanocomposites formed by two oxides as well as of oxides modified with metals as dopants or as embedded nanoparticles to obtain semiconductors with better photocatalytic properties. In this work it is reported the preparation of TiO₂ with MoO₃ nanostructures using a modified sol-gel technique. It is worth noting that Molybdenum trioxide has been investigated as photocatalyst due to its efficient absorption of most of UV and part of visible light being used as photosensitizer in composite photocatalytic systems [5].

2. Experimental Procedure

Molybdenum-based nanostructures were prepared by laser irradiation of powders in liquid medium. High purity MoO₃ powder (99.9%) was placed in a Pyrex glass container adding 10 ml of isopropyl alcohol. The MoO₃ particles were suspended in the liquid by stirring. The powder-alcohol mixture was irradiated with the unfocused beam of a Nd:YAG laser emitting at the fundamental line (1064 nm). The irradiation time was of 5 min and the energy per laser pulse was 80 mJ. To prepare colloids with different concentrations of nanostructures, the amount of powder was varied between 10 and 60 mg, obtaining concentrations of 80, 128, 250, 500, 754 and 1090 µg / ml.

Thin films were deposited by the spin coating method spreading the precursor solutions, prepared by the sol-gel technique, onto glass substrates at 3000 rpm using a spin coater KW-4A from Chemat Technology. The precursor solutions were prepared by the sol-gel technique with titanium isopropoxide (Ti[OCH(CH₃)₂]₄, Aldrich 97%), nitric acid (HNO₃, Fermont 70%) and 2-propanol (CH₃CHOHCH₃, Fermont 99.8%). The synthesis was carried out under environmental conditions mixing 5 mL of 2-propanol with 0.75 mL of titanium isopropoxide under continuous stirring. Subsequently, the MoO₃ nanostructures were added continuing the stirring for 5 minutes, afterwards 1 mL of nitric acid was added to promote the transition of the sol to a gel like. This procedure has been reported before to prepare TiO₂ thin films modified with different metals [6, 7, 8].

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical bonding of the present elements in the samples. XPS spectra were acquired in the low- and high-resolution regimes with a K-Alpha Thermo Scientific XPS spectrometer. The adventitious carbon peak at 284.8 eV was used as the internal standard to compensate for sample charging. The microstructure of the films was characterized by Raman spectroscopy, the spectra were obtained using a micro-Raman LabRam 800 system, equipped with a confocal microscope Olympus BX40 and a 100X objective, the samples were excited using the second harmonic of a Nd: YAG laser (532 nm). Optical measurements were performed utilizing a Perkin Elmer Lambda 35 UV/Vis spectrophotometer to obtain the transmittance spectra of the films from 200 to 1100 nm. Photoluminescence properties of the thin films were studied by PL spectroscopy using a spectrofluorometer FluoroMax 4 from Horiba Jobyn Ivon equipped with a 150 W Xenon lamp as excitation source. Scanning Electron Microscopy (SEM) was used to observe the morphology of the Mo nanostructures and the surface morphology of the films with a JEOL JSM-5900-LV microscope.

3. Results and Discussion

3.1 MoO₃ nanostructures characterization

The obtained Mo-based colloids showed a blue coloration [9] as is seen in figure 1a being darker for the more concentrated colloids. It is worth mentioning that the colloids are very stable and remain without changes one year after their preparation. The SEM image of the most concentrated colloid is shown in figure 1b, it is clearly seen that nanostructures with flake-like shapes are obtained. Lateral sizes are in the range from approximately 1.75 to 2.25 µm with thickness in the nanometer scale. The prepared Mo colloids were characterized by Raman spectroscopy. For this purpose, a drop of each of

the prepared colloids was deposited on pieces of silicon wafers. In general terms all the samples showed very similar spectra as the shown in figure 1c corresponding to the most concentrated colloid. It shows peaks at 115, 128, 157, 197, 217, 283, 290, 337, 365, 666, 819 and 995 cm^{-1} which agrees very well with the lattice vibrations of polycrystalline MoO_3 [10]. These results indicate that MoO_3 layered nanostructures form the prepared colloidal solutions.

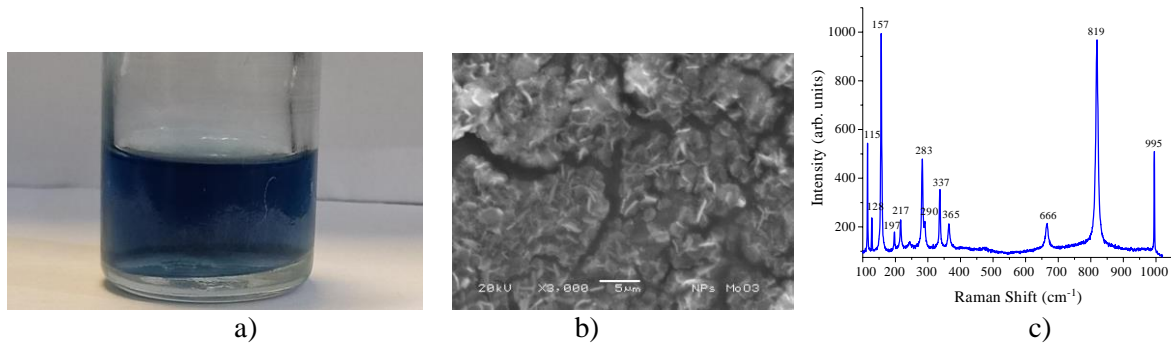


Figure 1. a) colloid prepared using 30 mg of MoO_3 powder, b) SEM image of the MoO_3 nanostructures prepared, c) Raman spectrum of the MoO_3 nanostructures

3.2 Thin films characterization

3.2.1 XPS characterization.

XPS measurements were performed for all films to determine the chemical bonding of the elements present in the films. Figure 2 shows representative XPS high-resolution spectra for the regions corresponding to Ti2p, O1s and Mo3d. The Ti2p spectrum (figure 2a) shows a doublet peaking at 464.2 and 458.6 eV that agrees well with Ti^{4+} in Ti-O bonds of TiO_2 [11]. The high-resolution XPS spectrum of the O1s region shows an asymmetric peak with a tail extending to high energies. The spectrum was fitted using Voigt line shapes which are shown in figure 2b. The most intense peak at 529.8 eV is attributed to O^{2-} species indicating the presence of TiO_2 [10]. The peak at 531.0 eV is attributed to a Mo-O bonding whereas the peak at 532.2 eV is attributed to C-O bonding [12] due to adsorbed surface contaminants from the atmosphere. Figure 2c shows the Mo3d region with peaks at 235.6 and 232.5 eV assigned to Mo^{6+} in Mo-O bonds of MoO_3 . These results reveal that the films are forming composites in which nanostructures of molybdenum trioxide are incorporated in the Titania matrix.

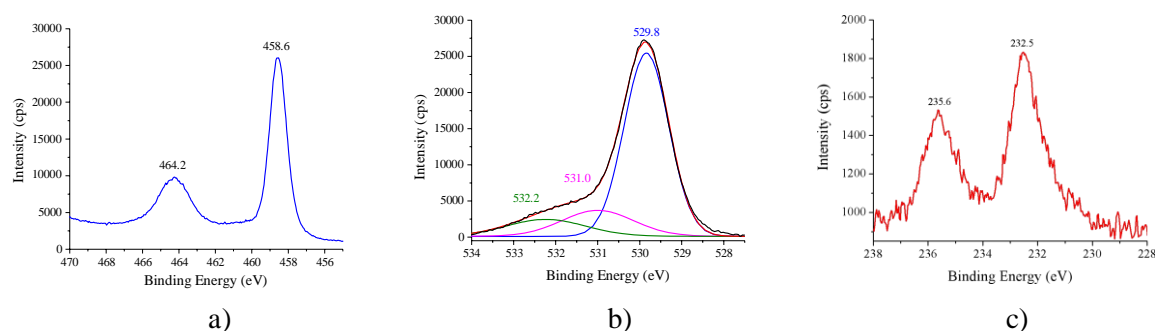


Figure 2. High resolution XPS spectra of the a) Ti2p, b) O1s and c) Mo3d regions

3.2.2 Raman characterization.

Raman spectra corresponding to different films are shown in figure 3. These display vibrational features at 142, 198, 395, 515, and 638 cm^{-1} characteristics of the anatase phase of titania [13]. In general terms these reveal that the anatase phase is present in all samples without any effect due to the

incorporation of the MoO₃ nanostructures probably due to the low loads of this oxide in the titania films.

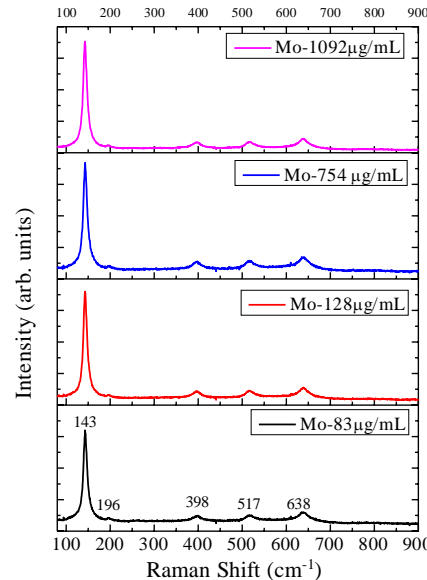


Figure 3. Raman spectra of films with different concentration of MoO₃ nanostructures

3.2.3 UV-Vis characterization.

Figure 4a shows the transmittance spectra corresponding to the films with a different amount of MoO₃ nanostructures. The transmittance spectra exhibit a similar absorption edge indicating that the deposited films have similar optical properties. Additionally, maxima and minima in the region from 400 to 1000 nm due to interference effects are seen. From the position and the corresponding transmittance of these maxima and minima an estimation of the thickness and refractive index were determined using the Goodman model [14]. The thicknesses were found from 108 to 155 nm whereas the refractive index values vary from 2.1 to 2.4. It is important to point out that the uncertainties of these values could be high because only one maximum and minima consecutives are present in the spectra. The bandgap energy of the thin films was determined using the Tauc method assuming indirect transitions. This was done plotting $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ as it is shown in figure 4b. The Eg values were obtained by a linear fit of the linear portion of the curve, determining its intersection with the photon energy axis as the quotient of the intercept to the slope. The obtained values were found to vary from 3.3 to 3.5 eV.

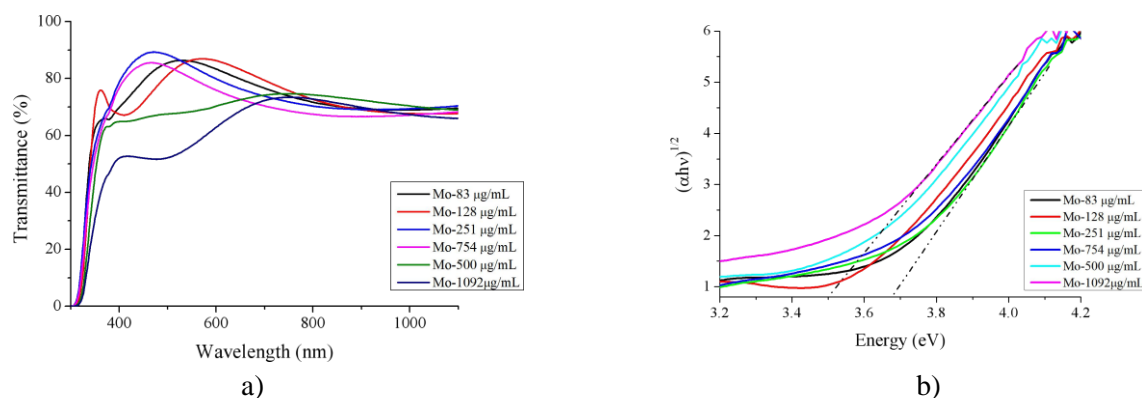


Figure 4. a) Transmittance spectra of thin films with different MoO₃ load, b) Tauc plots used to determine the band gap values

3.2.4 PL characterization.

Figure 5 shows the PL spectra of films with different load of Mo nanostructures. The PL spectrum of the TiO_2 film without Mo consist of a broad emission band from 350 to 500 nm, the maximum of emission, peaking at 380 nm (3.2 eV), can be attributed to an interband transition in good agreement with the anatase band gap value. The PL signal at 450 nm can be attributed to band edge free excitons whereas the peak at 470 nm can be assigned to bound excitons [15]. The high intensity of the PL signal indicates a high recombination rate of the photogenerated charges in TiO_2 . When MoO_3 nanostructures are incorporated in the titania, a strong quenching of the PL emission is observed; additionally, a new emission peak appears at 365 nm equivalent to 3.4 eV. These results reveal that PL emission depends strongly on the MoO_3 incorporation.

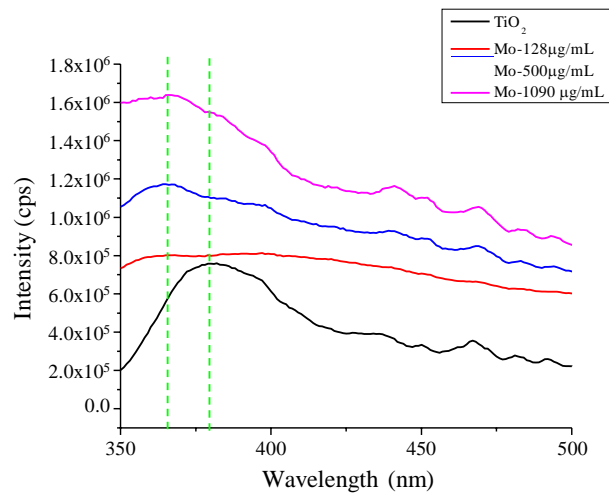


Figure 5. PL spectra of thin films with different MoO_3 load

3.2.5 Surface morphology.

A SEM image of the sample with the highest amount of MoO_3 nanostructures is displayed in figure 6. It is clearly seen that films have very smooth surfaces suggesting homogeneous lateral deposits. No effects on the surface morphology of the films due to the MoO_3 incorporation were observed.

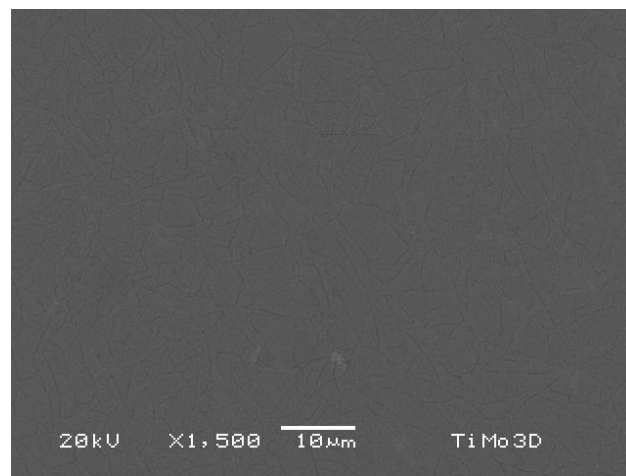


Figure 6. SEM image of the sample with the highest amount of MoO_3 nanostructures

4. Conclusions

Nanostructures with lamellar morphology were obtained by laser irradiation of MoO₃ powders suspended in liquid media. These nanostructures were incorporated in titania thin films through the sol-gel method. The characterization results reveal that the films are formed by composites in which nanostructures of molybdenum trioxide are incorporated in the titania film. Their physicochemical properties suggest their application as photocatalysts for the degradation of persistent organic molecules present in wastewaters.

Acknowledgements

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