

Synthesis and characterization of TiO_2 thin films doped with copper to be used in photocatalysis

Síntesis y caracterización de películas delgadas de TiO_2 dopadas con cobre para ser usadas en fotocatalisis

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Abstract— In this work we studied the influence of incorporation of copper into TiO_2 thin films on structural, optical and surface properties of TiO_2 thin films. The as-grown TiO_2 was synthesized by sol gel method using titanium isopropoxide, and the TiO_2 thin films were deposited by spin coating method. TiO_2 copper-doped ($\text{Cu}:\text{TiO}_2$) was synthesized by impregnation method using $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ as source of $\text{Cu}(\text{II})$, the $\text{Cu}:\text{TiO}_2$ thin films were deposited by spin coating method. The properties of the compounds obtained were evaluated by measurements of X-ray diffraction (XRD) and diffuse reflectance. The XRD results showed that Cu doping change the crystalline phase ratio of the films, XRD pattern of TiO_2 indicated that films grow with anatase structure, while $\text{Cu}:\text{TiO}_2$ thin films presented a polycrystalline mixture of anatase/rutile. Reflectance analysis indicated that TiO_2 presents an energy band gap of 3.25 eV and the $\text{Cu}:\text{TiO}_2$ presents a shift-red of the band gap to 2.9 eV. The results suggest that doping with copper improved the harvesting of the TiO_2 to visible radiation.

Keywords— TiO_2 , Photocatalysis, metal doping, X-Ray, Diffuse Reflectance.

I. INTRODUCTION

Nowadays the uncontrolled growth of the population increases both the water consumption and the amount of pollutants in the water resources;

water treatment is an important research topic around the world. The development of mechanisms of water treatment is a necessity because water is not a renewable resource [1]. In the last decades, advanced oxidation processes (AOPs) have presented different kinds of methodologies for remediation of water and heterogeneous photocatalysis have become a promising method for purification. In this field Titanium oxide (TiO_2) is one of the most important photocatalytic materials. There currently exists a better understanding and improvement of catalytic reactions, which is a main driving force for surface investigations on TiO_2 . However, two drawbacks limit the practical application of TiO_2 technology: (a) it is effective only under ultraviolet irradiation ($\lambda < 380 \text{ nm}$) and (b) the low-quantum efficiency of this process [2]. To solve these, different methodologies have been used: sensitization with organic dyes, natural and synthetic [3], metal ion implantation [4] noble metal loading [5], metal ion doping [6], anion doping [7], composite semiconductors [8]. All of these present both advantages and drawbacks, however, metal ion doping is one of

the most promising because it shifts the TiO₂ responses towards longer wavelengths and an enhanced photoactivity is obtained from incorporation of metallic dopants. These advantages can be explained because a dopant ion acts as an electron trap or hole trap; this could prolong the lifetime of the generated charge carriers, resulting in an enhancement of photocatalytic activity [9, 10]. The ionic metallic doping could be done through different ways such as hydrothermal precipitation [11], sol-gel [12], chemical vapor deposition [13], impregnation method [14] and sputtering [15]. The impregnation method has proven to be convenient for the modification of TiO₂ due to its low cost of implementation, the low synthesis temperatures, and because it easily allows the coating large areas.

In this work, we studied the influence of incorporation of Cu into TiO₂ on its structural, optical properties.

II. EXPERIMENTAL

A. Materials synthesis

The as-grown TiO₂ Thin films were synthesized by the sol-gel method for the as-grown TiO₂ synthesis, the titanium isopropoxide [Ti(OC₂H₅)₄] was used as reagent, ethanol (CH₃CH₂OH) and water were used as solvent and nitric acid (HNO₃) was used as buffer. The molar ratio was [CH₃CH₂OH:H₂O:HNO₃:Ti(OC₂H₅)₄] 55:1,5:0,3:1 respectively. The Cu:TiO₂ powder was obtained by adding copper (II) nitrate and titanium tetrachloride as source of copper and titanium respectively; furthermore, HCl was used as a buffer solution, a solution of cetyltrimethyl ammonium bromide (CATBr) was used as surfactant and water-ethanol mix was used as solvent in the following molar ratio [Ti:CATBr:HCl:H₂O:EtO:Cu] 1:0,16:1,7:1,7:20:0,025 respectively. The as-grown TiO₂ and the Cu:TiO₂ thin films were deposited on the substrates from a coating solution by spin-coating technique in a nitrogen atmosphere. The substrates coated with films were annealed at 450°C for 1 hour in air.

B. Characterization of materials synthesized

The X-ray powder diffraction (XRD) patterns were recorded in X-ray powder diffractometer (MSAL-XDII) using K_α radiation of the Cu (λ

=0,15406nm) for operating at a 30 kV voltage with a current of 20 mA. The optical properties of the as-grown TiO₂ and the Cu:TiO₂ thin films were studied through diffuse reflectance measurements. The diffuse reflectance absorption spectrum of the as-grown TiO₂ and the Cu:TiO₂ thin films were measured using a Lambda 4 Perkin Elmer spectrophotometer equipped with an integrating sphere. Kubelka-Munk model and analysis based on differential reflection spectra were used to independently determine the energies of the fundamental optical transitions. FT-IR spectra (KBr) of the compounds were recorded on a Bruker Tensor 27 spectrometer in the spectrum region of 3500-500 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Diffuse transmittance measurements

The optical properties of the as-grown TiO₂ thin film and Cu:TiO₂ thin films were determined from diffuse reflectance measurements in the range of 200–800 nm. Fig. 1(a) shows the diffuse reflectance spectra of the as-grown TiO₂ thin films, The results indicate that about 70% of the visible radiation is reflected in the visible range (after 350nm). Furthermore, a sharp absorption edge is observed near to the 340 nm, indicating the good crystallinity and a low defect density near to the band edge. This behavior is typical of thin films of TiO₂ [16]. The results of diffuse reflectance spectra were analyzed with Kubelka-Munk remission function, given by the equation below [17]:

$$F(R_{\alpha}) = \frac{(1 - R_{\alpha})^2}{2R_{\alpha}} \quad (1)$$

Where R_α is the reflectance and F(R_α) is proportional to the constant absorption of the material, an indicative of the absorbance of the sample in a particular wavelength. The optical band gap of the films was determined by extrapolating the linear portion of the (αhv)² versus hv plot on the x-axis [18].

$$(\alpha hv)^2 = A(hv - E_g) \quad (2)$$

Where E_g is the band gap energy and A is a constant depending on the transition probability.

Fig. 1. (a) DIFFUSE SPECTRA OF THE THIN FILMS. (b) $(\alpha h\nu)^{1/2}$ VS. $h\nu$ SPECTRA INDICATING THE VALUE OF EG FOR TiO_2 AND $\text{Cu}:\text{TiO}_2$ THIN FILMS

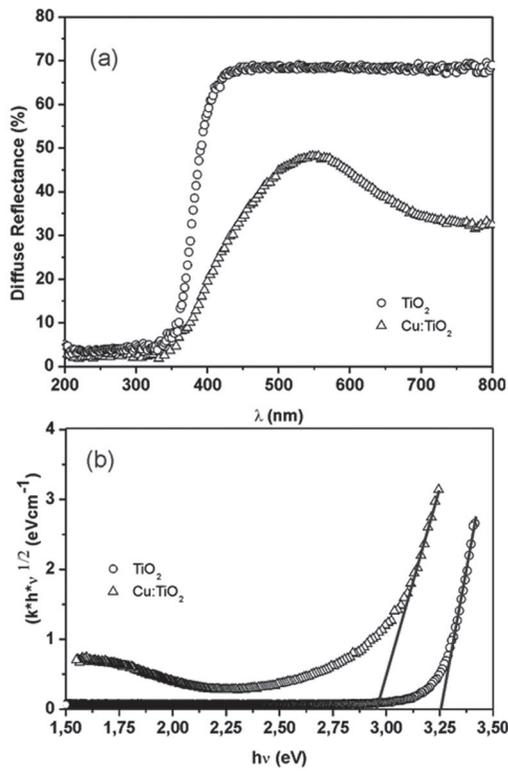
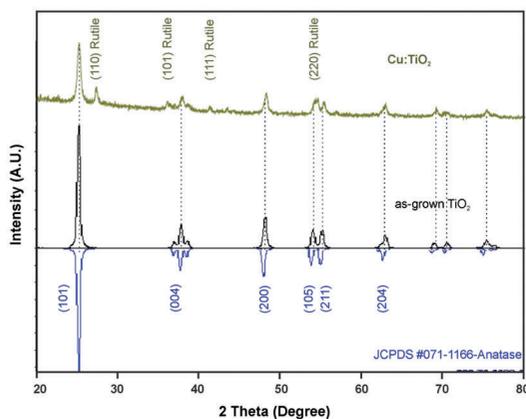


Fig.1(b) shows the $(\alpha h\nu)^2$ versus $h\nu$ for the as grown TiO_2 thin films and $\text{Cu}:\text{TiO}_2$ thin films

Fig. 2. XRD PATTERN OF TiO_2 THIN FILMS DEPOSITED BY SOL-GEL METHOD, TiO_2 CU-DOPED AND JCPD-ANATASE REFERENCE.



It is observed that the band gap of as-grown TiO_2 thin film was 3,25 eV, which corresponds to the typical value of energy of the anatase TiO_2 ; this

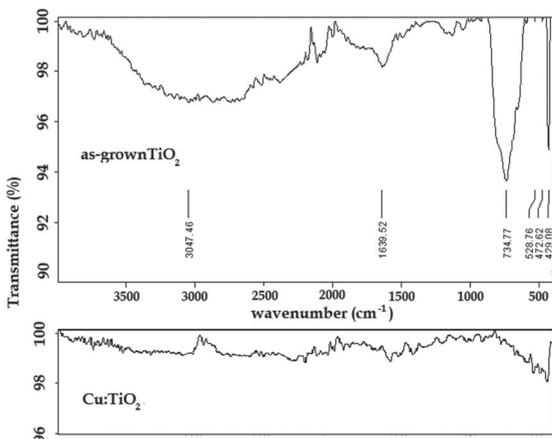
result is according to XRD measurements presented afterwards. The results also show a shift of absorption band edge towards visible region upon doping TiO_2 with copper, $\text{Cu}:\text{TiO}_2$ thin films present a band gap energy of 2,9 eV. These results suggest that copper could be incorporated into the crystalline TiO_2 network modifying its band structure and therefore its electrical properties. According to the optical results, it can be assumed that Cu-doping onto TiO_2 may enhance the visible-light absorption and it could improve the photocatalytic activity of TiO_2 .

B. XRD measurements

Fig. 2 shows experimental XRD pattern corresponding to as-grown TiO_2 thin films and the $\text{Cu}:\text{TiO}_2$ thin films deposited on soda lime glass substrates by spin coating. The XRD measurements show that as-grown TiO_2 thin films were polycrystalline and present only one crystalline phase corresponding to the anatase phase (Fig. 1 includes a JCPDS-#071-1166 pattern of reference), the pattern of as-grown TiO_2 thin films presents different planes of growth and all diffraction signals correspond to the anatase-pattern indicating that only one crystalline phase is present. Furthermore, XRD results showed that the as-grown TiO_2 thin films grow in a preferential orientation in the crystalline plane (110), typical of the anatase phase. These results could occur due to the method used to obtain the compound, according to other reports [19]. Fig. 2 also shows the XRD pattern of the $\text{Cu}:\text{TiO}_2$. The diffraction pattern shows three additional diffraction signals at $2\theta=27,9$, $2\theta=37,9$, $2\theta=42,4$, $2\theta=56,9$; these reflections can be associated with the planes (110), (101), (111) and (220) respectively. These crystalline planes can be associated with the rutile phase (JCPDS #021-1276); this happens because the rutile phase is thermodynamically the most stable crystalline phase and it possesses the highest density with a compact atomic structure. The presence of Cu is a disadvantage for the formation of the metastable anatase phase and so the rutile growth can occur [20]. Furthermore, not a signal associated with CuO or compound of Cu is observed, indicating that the compound could be amorphous or that it could be incorporated in the crystalline network of the doped TiO_2 . However, the change in the way of the crystalline growth indicates that the Cu parti-

icipates in the growth of the TiO₂ and it could be incorporated in the crystalline network of the final compound according to other reports. This assertion is confirmed for optical results [21].

Fig. 3. IR-SPECTRA OF THE AS-GROWN TiO₂ AND Cu:TiO₂ THIN FILMS



C. IR measurements

Fig. 3 shows the IR-spectra of the as-grown TiO₂ films annealed at 500 °C. The chemical bonding of the powders was scrutinized by correlating the developed peaks in the spectrum to the vibration or stretching of various functional groups. Results show two strong absorption signals in the frequency region of 429,1 cm⁻¹ and 734,7 cm⁻¹ corresponds to Ti-O-Ti bonding and indicates the formation of a titanium oxide network [22], furthermore, a broad band at 3400 cm⁻¹ is observed, which is characteristic of associated hydroxyl groups (absorbed molecular water), weakly chemisorbed and disappearing at temperatures of 200 °C; a corresponding weak bending vibration band at near 1630 cm⁻¹ is also observed [23]. Finally, fig 3 shows the IR spectra of the Cu:TiO₂ thin films. In these spectra the intensity of the signals of TiO₂ decrease significantly, indicating that water has been desorbed and not a signal associated to the stretching mode of Cu-O is detected, which demonstrates that copper could have been incorporated into the TiO₂ network as proved by the optical results.

III. CONCLUSIONS

Thin films of TiO₂ were doped with copper and the optical and structural properties were investigated. The optical results indicated that TiO₂ do-

ped with copper presents a red-shift of the transmittance spectra increasing the absorption of the photocatalyst in the visible region. The band gap increased by about 12% from 3.25 eV TiO₂ to 2,9 eV TiO₂ doped with copper. The XRD analysis showed that TiO₂ grows in the anatase phase while thin films of TiO₂ doped with copper present a polycrystalline mixture of anatase, rutile, and brookite. Results indicated that TiO₂ doped with copper can be used as an active photocatalyst in a visible range of the electromagnetic spectra.

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