World Journal of Environmental Research

Volume 7, Issue 2, (2017)88-97

www.wjer.eu

Influence of the number of layers on photocatalysis activity of TiO_2 thin films

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Suggested Citation:
Boutelala, A., Bourfaa, F. & Mahtali, M. (2015). Influence of number of layers on photocatalysis activity of TiO_2 thin films. *World Journal on Environmental Research*. *7*(2), 88-97.

Received June 27, 2017; revised September 10, 2017; accepted December 5, 2017.
Selection and peer review under responsibility of Prof. Dr. Haluk Soran, Near East University.

Abstract

Titanium oxide (TiO_2) is one of the most important semiconductors because of their properties. This study was carried out to investigate the influence of the number of layers of Co-doped TiO_2 thin films obtained by sol–gel method on the photocatalytic activity. The crystalline structure of films is characterised by means of X-ray diffraction and Raman spectroscopy. All the films were of anatase phase and the particle size was in nanoscale. The surface morphology was studied by atomic force microscopy. The optical properties were investigated by UV-visible spectroscopy. The photocatalytic properties of the samples were tested on the degradation of methylene blue dye solution. The results indicated that photocatalysis is more important when the number of dipping of films increases.

Keywords: Photocatalysis, X-ray diffraction, TiO_2, thin films, methylene blue.

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1. Introduction

In recent years, titanium dioxide has been the subject of much research, because it is a cheap material, non-toxic and has great chemical and mechanical stability. Moreover, it also has a high refractive index and a high transmittance in the field of visible light, which makes it a very attractive compound in more than one field of optical applications. The increased interest in this material is due in part to its unique photocatalytic properties. It is well known that titanium oxide (TiO_2) has strong photocatalytic abilities to purify pollutants in air and water under UV irradiation (Buechler, Noble, Koval & Jacoby, 1999; Konstantinou, Sakellarides, Sakkas & Albanis, 2001). Many studies are based on TiO_2 as powder (P25) on photocatalysis activity (Krishnan et al., 2017; Yu, Yu, Cheng, Zhou & Zhao, 2006). But TiO_2 powder slurries have the disadvantage of requiring stirring during the reaction process and are difficult to separate out after the reaction. TiO_2 thin films can overcome these disadvantages (Rodrıguez, Gomez, Lindquist & Granqvist, 2000). The aim of this survey is to understand the fundamental processes and improve the photocatalysis efficiency of TiO_2 as catalyst (Hoffmann, Martin, Choi & Bahnemann, 1995; Linsebigler, Lu & Yates, 1995; Wang, Zheng, Hao & Wang, 2002).

Photocatalysis is a science of employing a catalyst to speed up chemical reactions that require or engage light. A photocatalyst is defined as a material that is capable of absorbing light, producing electron–hole pairs that enable chemical transformations of the reaction participants and regenerate its chemical composition after each cycle of such interactions (Bahnemann et al., 1995; Chan, Wu, Juan & Teh, 2011; Djurisic, Leung & Ng, 2014; Hernández-Ramírez & Medina-Ramírez, 2015; Hisatomi, Kubota & Domen, 2014; Pelizzetti & Minero, 1994).

Metal oxides such as oxides of vanadium, chromium, titanium, zinc, tin and cerium having these characteristics follow similar primary photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidise organic substrates (Bahnemann et al., 1995; Domen et al., 2014; Hernández-Ramírez & Medina-Ramírez, 2015).

In the present work, we have studied the photocatalysis application of TiO_2 thin films with various dipping prepared by sol–gel method, to study the degradation of methylene blue (MB) with a concentration of 10^{-5} mole/l. The obtained 3% TiO_2 thin films doping cobalt with different layers were characterised by means of X-ray diffraction (XRD) and Raman spectroscopy. The surface morphology was studied by means of atomic force microscopy (AFM). UV–visible absorbance of the films was performed by Shimadzu UV–3101 PC spectrophotometer within the wavelength range of 500–700 nm.

2. Experiment Details

TiO_2 thin films-doped cobalt were deposited on microscope glass as substrate after cleaning by acetone, ethanol and distilled water for 10 min for each one by ultrasonic bath. We used the sol–gel dip coating as a method for deposition films with different layers from 1 to 4 layers and the concentration of cobalt was fixed at 3%. The obtained films were annealed in the furnace at 500 °C for 2 hours.

The crystalline structure and phase of the films were measured using XRD with a Cu Kα source under an applied voltage of 40 kV and a current of 40 mA. The crystallite size was determined from the XRD pattern. The optical properties of films were monitored on UV-Vis-NIR spectrophotometer. The photocatalytic activity of the films was determined by the decomposition of MB dye solution: TiO_2 thin film was doped at 3% Co with different layers.

The lamp used as the UV source in photocatalysis activity had a centre wavelength at 254 nm.

3. Results and Discussion

3.1. Film structure

TiO_2 has three different crystal structures: rutile, brookite and anatase. Both brookite and anatase are metastable over a wide temperature range (Ding & Liu, 1998), while the rutile phase is only stable. TiO_2 is widely used as thin films with anatase and rutile phases in photocatalysis activity, but anatase has more efficiency than rutile in this application (Hao et al., 2002). TiO_2 thin films with anatase tetragonal structure show high photocatalytic activity (Linsebigler et al., 1995).

The crystalline structure of TiO_2 thin films doped at 3% Co with various layers from 1 to 4 layers and annealed at 500 °C, is shown in Figure 1. It is evident that all the samples are completely anatase phased with (101) as plane.

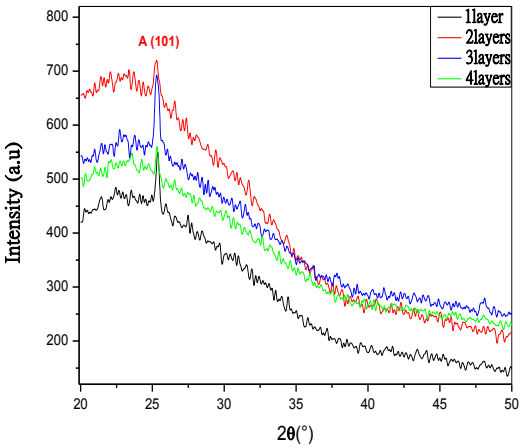

Figure 1. XRD pattern of 3% TiO_2 doped Co at 500 °C with different dipping

The crystallite size of a polycrystalline films was calculated using the formula of Scherer (Chen, Kelder & Schoonman, 1999):

$$D = (0.94\ \lambda)/\beta(\cos\ \theta) \quad (1)$$

where D is the mean dimension of the crystalline perpendicular to the planes (h k l), β is the full-width at half-maximum intensity in radians, θ is the Bragg angle and λ is the wavelength of the used X-rays.

In Figure 2, the crystallite size of all samples is presented. It is observed that the crystallite size decreases from 1 to 2 layers, then increases with increase in the number of layers (3 and 4). As can be seen, the crystallite size of films with anatase phase range from 6 to 17 nm, so we are in good agreement with Diana Mardare, Tasca, Delibas, and Rusu (2000), who report that the crystallite size of TiO_2 thin films vary between 7 and 28 nm.

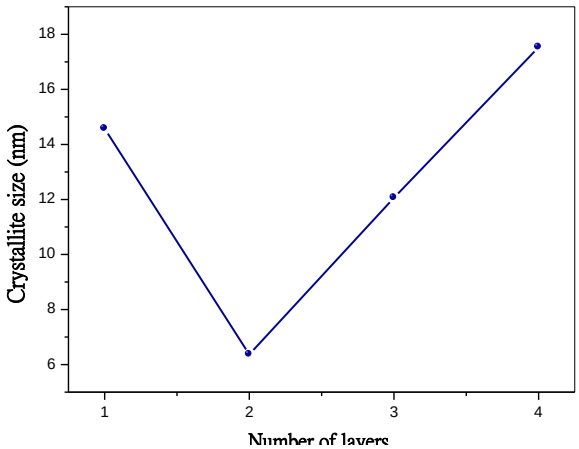

Figure 2. Crystallite size of 3% TiO_2 doped Co at 500 °C

Figure 3 shows the Raman spectra as prepared with 3% TiO_2 thin films doped Co with various numbers of dipping (1–4 layers). The Raman spectrum for anatase TiO_2 was identified by Ohsaka, Yamahoka, and Shimomura (1979) at 144 cm^{-1} (Eg), 197 cm^{-1} (Eg), 399 cm^{-1} (B1g), 513 cm^{-1} (A1g), 519 cm^{-1} (B1g) and 639 cm^{-1} (Eg).

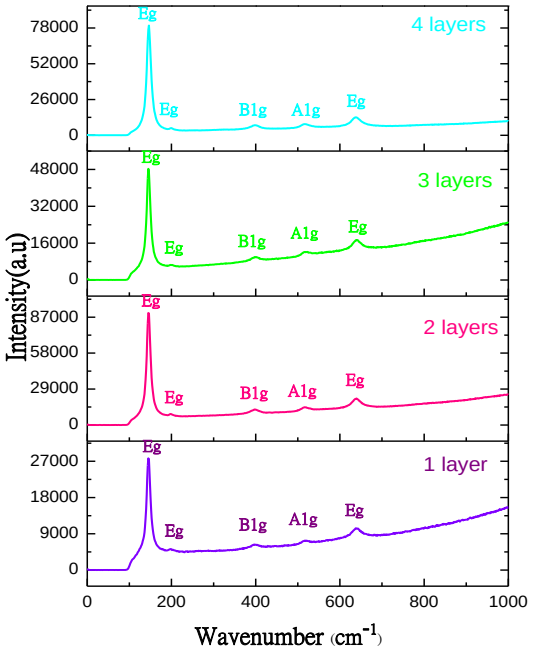

Figure 3. Raman spectra of 3% Co-doped TiO_2 thin films obtained after various dipping

The Raman spectra are composed with three main photon modes Eg, B1g and A1g for all the samples.

As shown in Figure 3, these modes are located at 145, 8; 199, 33; 399, 515, 78 and 638 cm^{-1}.

These signals are characteristic of the anatase phase of TiO_2 (Mechiakh, Ben Sedrine, Ben Naceur & Chtourou, 2011). The samples with two layers show the presence of the predominant anatase crystalline structure.

As observed, there are no peaks related to the phase rutile, which indicates that the films obtained have a pure anatase structure. The Raman data are in good agreement with the XRD results.

3.2. Surface morphology

Confirmation of the crystallisation process studied by XRD and Raman was carried out by AFM observation and the experimental results are shown in Figure 4.

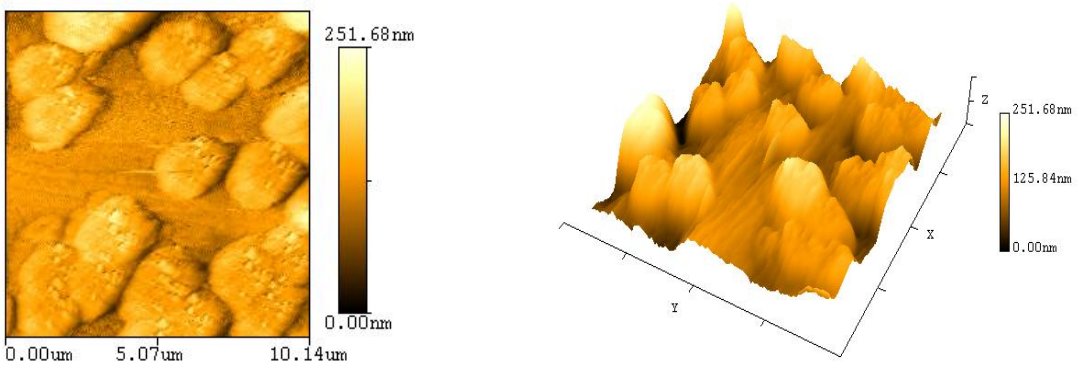

Figure 4. AFM image (2D and 3D) of TiO_2 with 3% Co and 4 dipping at 500 °C

In Figure 4(a and b) is presented typical 2D and 3D AFM image of TiO_2 film deposited on glass substrate. The (3D) image indicates that the film surface exhibits hills and valley-like structures, which are uniformly distributed over the entire substrate surface. The 2D images show a compact and granular morphology with the presence of pores on the surface; this benefits the degradation of the MB dye solution. The root-mean square roughness of this film is equal to 34, 70 nm. So the surface film is so rough.Porous materials have been extensively investigated and it is well recognised that porous material, due to their high specific surface, is most suitable for application in the fields of photocatalysis and gas sensing (Lamri Zeggar, Bourfaa, Adjimi, Aida & Attaf, 2016).

3.3. Optical properties

The transmittance spectrum in the UV-visible region of the prepared 3% TiO_2 films doped Co with various dipping in wavelength ranged from 300 to 900m is shown in Figure 5.

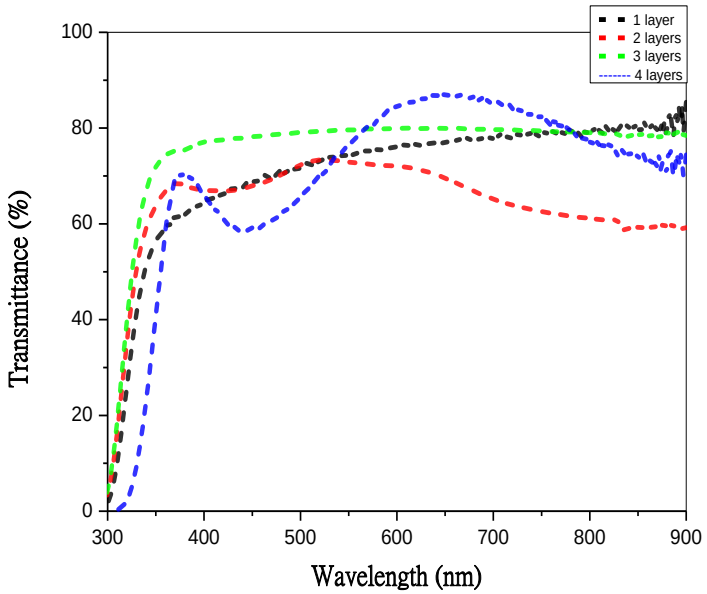

Figure 5. Transmittance spectrum of TiO_2 thin films with different dipping

As can be seen, the films obtained after various dipping have a high transmittance of 85%. The higher transmittance of the doped samples can be correlated with their having pure anatase structures (with lower density and refractive index)

These spectra show that the films are transparent in the visible and opaque in the ultraviolet. We also note that increase in the number of dipping leads to a shift of the fluctuation bands towards the short wavelengths. These are a consequence of the increase in grain size.

3.4. Photocatalytic activity

We have studied the variation of absorbance spectra of MB solution after different UV light exposure times. The wavelength region is ranged from 500 to 700 nm. The absorption peak intensity is used as a signature for dye degradation. From the variation of this absorption peak with exposure time, we concluded that photo degradation is more significant when the solution is in contact with films for four dipping.

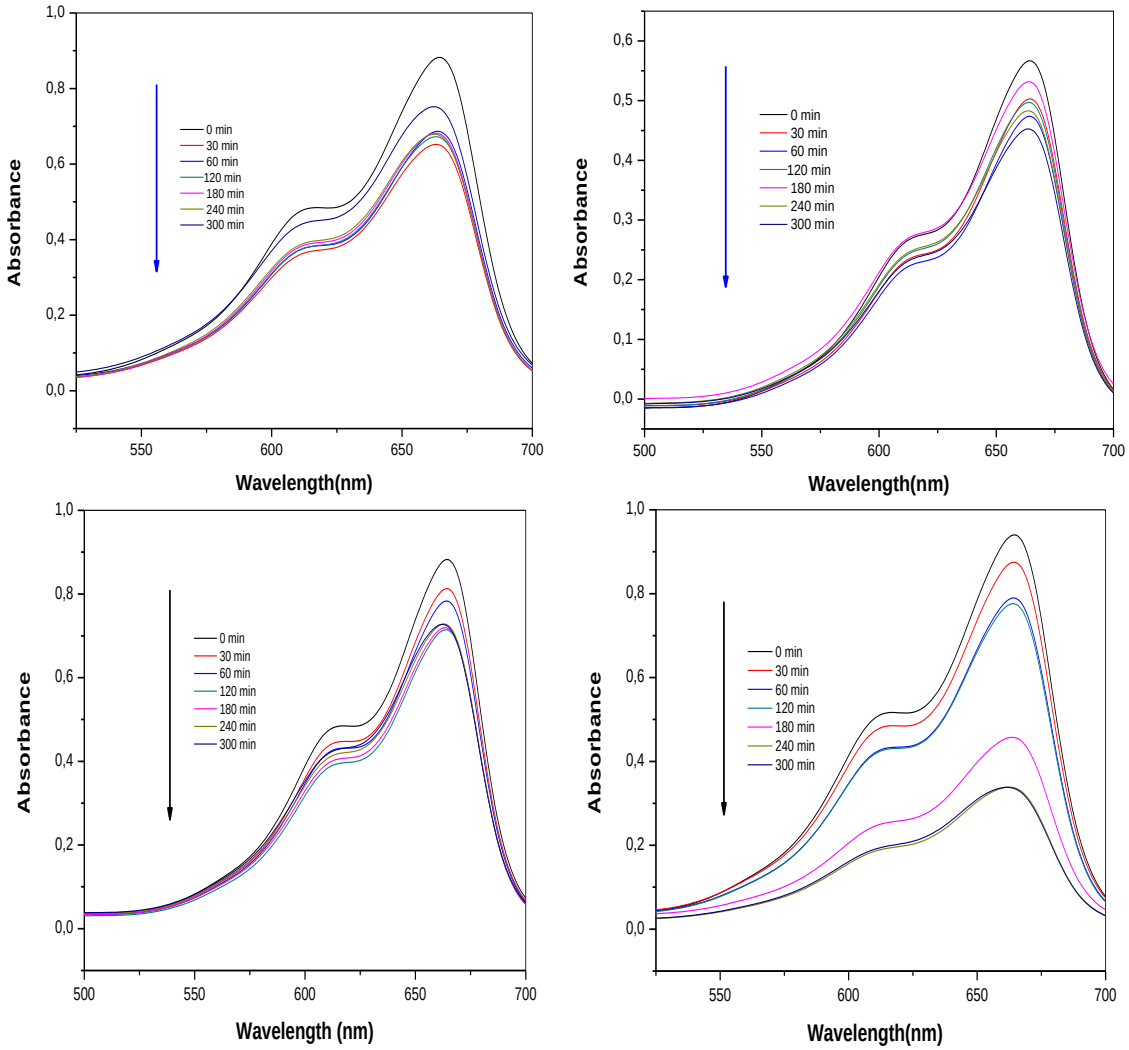

Figure 6. Variation of the absorbance of the MB solution as a function of the wavelength of 3% TiO2 doped Co with various dipping films: (a) one dipping; (b) two dipping; (c) three dipping; and (d) four dipping

Here, MB was adopted to evaluate the photocatalytic activities of the samples. Figure 6 shows reduction of MB dye concentration with reaction time (*t*) for sample one dipping, two dipping, three

dipping and four dipping on photocatalytic thin films. The sharp decrease in the first 30 min is due to the adsorption of MB onto the thin films. Colour change in the MB solution indicated that there must be some chemical reactions occurring. From Figure 6 it can be seen that the sample with four dipping showed a higher photocatalytic activity than the other samples.

To have more insight into the photo degradation kinetics and the influence of the number dipping of Co-doped TiO_2 thin films, we monitored the variation of the intensity of the absorption located at 664 nm. Figure 7 shows the variation of the ratio C/C_0, where C is the peak intensity at time t and C_0 is the peak intensity before light exposure.

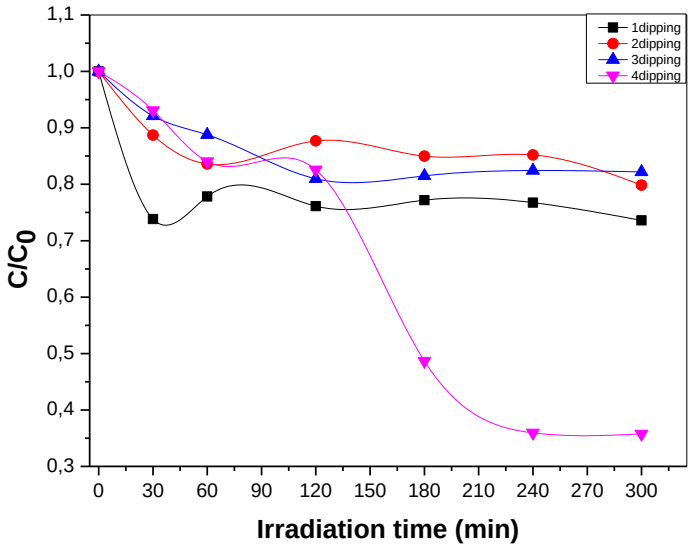

Figure 7. Photo degradation kinetic of MB pollutant by all the TiO_2 thin films.

As can be seen, photo degradation is more important when using film obtained with four dipping; the ratio is reduced with increasing exposure time; it reaches 0.35 after 300 min of irradiation. However, in the cases of three dipping, two dipping and one dipping of films obtained, the ratio is slightly reduced up to 0.82; 0.79 and 0.73 after 300 min, respectively. As shown, the photocatalytic decomposition of MB pollutant, in contact with the surface of TiO_2 thin films with all the dipping, follow a pseudo first-order kinetic law, and can be expressed as (Li & Wang, 2010):

$$-\mathrm{Ln}\,(C/C_0) = kt \qquad (2)$$

where C and C_0 are the reactant concentration at time t and $t = 0$, respectively and k rate constant (reaction rate constant) (Li & Wang, 2010). In Table 1 is given the calculated value of rate k for all the TiO_2 thin films. TiO_2 doped at 3% Co with four dipping is characterised by a larger rate k than the other films. Thus, it was concluded that the TiO_2 film with four dipping possessed higher photocatalytic activity than the other film.

Table 1. Degradation rate k and conversion rate of TiO_2 thin films deposited with different dipping

3% Co-doped TiO_2	Degradation rate k(min-1) × 10−4	Conversion rate (%)
One dipping	5	27
Two dipping	4	21
Three dipping	6	18
Four dipping	39	65

The conversion rate defined as

$$\tau = (C_0 - C(t)/C_0) \times 100 \quad (3)$$

is an interesting quantity that can yield information about the pollutant degradation, and represents the relative quantity of removed pollutant from the solution.

Figure 8 illustrates the variation of the conversion rate obtained with all TiO_2 thin films. In the case of four dipping, 65% of pollutant is removed after 300 min of exposure time, while only less than 18%, 21% and 27% are removed when using three dipping, two dipping and one dipping as a film, respectively. In this case, we can explain this variation in degradation rate by taking into account the following parameters: the morphology of the TiO_2 layer, thickness and porosity of the deposited layer. It is clear that all these parameters play a very important role in the efficiency of the photocatalytic activity.

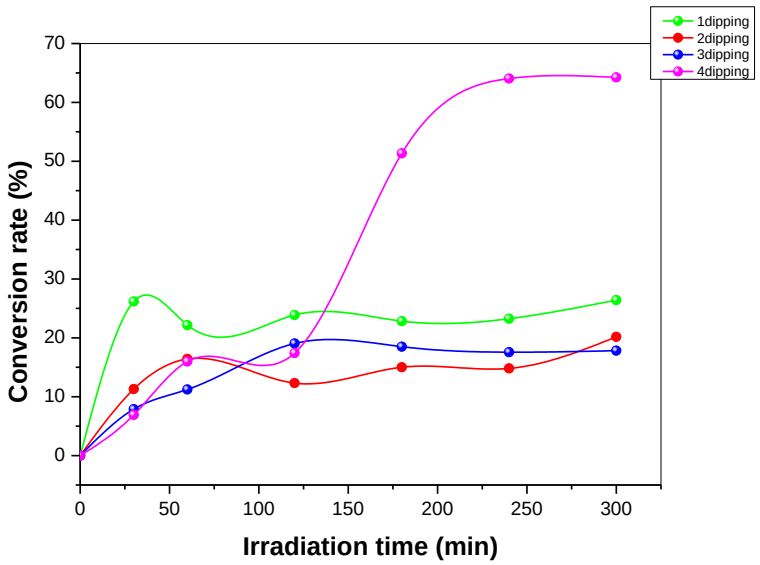

Figure 8. Evolution temporal of the conversion rate of MB pollutant during its degradation in contact with TiO_2 thin films deposited by various dipping

Increasing the specific reactive surface and reducing the size of TiO_2 also increases photocatalysis efficiency (Calza, Pelizzetti, Mogyorósi, Kun & Dékány, 2007; Hadj Salah, Bouhelassa, Bekkouche & Boultif, 2004).

The discrepancy in the photocatalysis activity of all thin films of TiO_2 may found explication in the difference between their morphology. As deduced from the AFM images, the sample of four dipping is rough and has pores on the surface with a granular surface morphology.

Generally, the smaller particle size and the higher photocatalytic activity were investigated by Anpo, Shima, Kodama, and Kubokawa (1987). They reported that with anatase of small TiO_2 particle size, the high photocatalytic activity for hydrogenation of CH_3CCH with H_2O had been obtained.

Hou, Huang, Wu, and Liu (2009) mentioned that with increase in the time of irradiation, the activity of the TiO_2/Ag catalyst decreases gradually and Ag does not have an effect on photocatalysis. The decomposition rate (k) at a maximum of 0.0014 min^{-1} is observed, while in our study the degradation rate k is ranged between 0.0004 and 0.0039 min^{-1}.

4. Conclusion

Transparent 3% TiO_2 thin films doped Co have been prepared on microscope glass by the sol–gel method. The number of dipping of films influenced the photocatalytic activity. The samples are all in the complete anatase phase and the particle size is in nanometre scale. Raman spectra showed that all

the main photon modes are characteristic of the anatase phase of TiO_2. The surface morphology of the sample with four dipping is rough in the presence of pores in the surface. The sample prepared with four dipping shows the higher photocatalytic activity and the large degradation rate *k*. From this survey, we conclude that extensively investigated porous materials have shown that due to their high specific surface, they are most suitable for application in the fields of photocatalysis and gas sensing.

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