Photocatalytic activity of Al/Ni-doped TiO₂ films synthesized by sol-gel method: Effect of sunlight photocatalysis on the catalysts properties

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Abstract

Photocatalytic activity of semiconductors is affected by the nature of metal dopant. To study the effect of non-transition and transition metal on the physical and optical properties of TiO₂ based photocatalysts; Al and Ni-doped TiO₂ thin films respectively were prepared via a sol-gel dip-coating method. The effect of the photocatalysis process on the properties of TiO₂ based thin films was investigated. The photocatalytic activity was calculated from methylene blue dye degradation under sunlight irradiation. XRD results show that un-doped TiO₂ films were grown with anatase phase, whereas, the Ni and Ni/Al-doped TiO₂ films show Ti₄O₇ single phase. The presence of Al preferred the rutile phase. No phases related to NiO or Al₂O₃ were detected. Ni-TiO₂ photocatalyst shows high photocatalytic activity (~93%) thanks to the high content of O and Ti, wide bandgap (3.35 eV), low crystal size (6.87 nm), high film thickness (288 nm), and high surface roughness (44.5 nm). After photocatalysis, all the films show a decrease in O content and thickness, whereas the indirect bandgap values were increased which suggesting the reuse with low photocatalytic activity.

Keywords:
Al, Ni doped TiO₂; Thin films; Sol gel; Methylene blue; Photocatalysis; Sunlight.

1. Introduction

Titanium dioxide TiO₂ is a versatile transition-metal oxide that has a large number of applications such as protective coatings [1-2], Photodetector [3], optical thin films [4-5], microelectronic devices [6], self-cleaning [7-9], and photocatalyst for the breakdown of organic contaminants in wastewaters [10-13]. All these applications are a traduction of their attractive properties such as high transmission in the visible region, wide band gap for anatase phase (3.4 eV), and high photocatalytic activity under UV light [14].
As well known, there is two technologic ways for the illumination of organic substances from wastewater by the heterogeneous photocatalytic processes, i.e. suspended and fixed type. The suspended photocatalyst has more active surface sites than the fixed one due to its movement and nature of the material used (powder); however, its separation from treated solution is an issue[15]. The fixed photocatalyst has an advantage to mostly employ as thin films that are easy to use on an industrial scale at low cost.

In recent years, variety of researches have involved studying the photocatalytic properties of TiO$_2$ thin films exposed under sunlight[16-18] and UV light radiations[19-21]. Wen et al.[22] studied the effect of doping TiO$_2$ catalyst by I and F on the degradation rate of methylene blue and disclosed that TiO$_2$ photocatalyst exhibited much higher activity under UV light than that under simulated sunlight. Yu et al.[23] reported that the photocatalytic activity of TiO$_2$ thin film was remarkably enhanced by Ni doping at 0.5 at. % dopant concentration. The general mechanism of TiO$_2$ semiconductor photocatalysis is described step by step in the literature[24, 25].

In this study, we purposed a cost-effective solution within the fields of wastewater treatment before putting it up. Aluminum and Nickel doped TiO$_2$ photocatalyst thin films were synthesized on glass substrates by sol-gel dip-coating technique and then characterized. Al and Ni are chosen as non-transition and transition metal respectively, to study the effect of metal doped TiO$_2$ thin films on the photodegradation rate of methylene blue dye under sunlight irradiation.

2. Experimental details

2.1. Materials

All chemicals were used as received from Sigma Aldrich without any purification. Double distilled water was used for all experiments. Sol-gel dip coating technique was used for the synthesis of Al/Ni/TiO$_2$ thin films. Titanium (IV) isopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$], Nickel (II) nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O], and Aluminum nitrate nonahydrate [Al(NO$_3$)$_3$.9H$_2$O] were used as the precursor materials for TiO$_2$, Ni, and Al respectively. Water, isopropanol and ethanol were functioned as solvents. Glacial acetic acid was used as a chelating agent.

2.2. Titanium dioxide-Ni-Al thin films synthesis

The sol has been formed by dissolving TTIP in water and isopropanol (iPrOH) then stirred for 30 min. Later, Glacial acetic acid was added dropwise into the sol with vigorous stirring for 2 h at room temperature. The molar ratio of the components was optimized at H$_2$O: iPrOH: TTIP: Glacial acetic acid = 2:25:1:1. The final solution is a transparent yellowish. To synthesis Al and Ni doped TiO$_2$ thin films, Nickel (II) nitrate hexahydrate (Ni 3 wt. %) and Aluminum nitrate nonahydrate (Al 3 wt. %) were dissolved in 10 ml ethanol for 60 min and then added to the previous solution respectively.
Glass substrates were cleaned in acetone for 5 min to avoid any organic contamination and then washed with ethanol and water. The substrates were dipped in the prepared solutions for 30 seconds, and then withdrawn at a speed of 0.8 mm.s\(^{-1}\) and dried at 100 °C for 5 min to evaporate organic solvents. The dip-coating procedure was repeated five times. All the TiO\(_2\) based thin films were calcined at 450 °C for 3 hours.

### 2.3. Al/Ni/TiO\(_2\) thin films characterization

The crystallographic structure of the films was evaluated by X-ray diffraction using a Bruker diffractometer (D8 Advance model) with CuKa radiation (\(\lambda=1.5406\) Å), scanning from 20–80° at a rate of 0.03° s\(^{-1}\). The 3D surface topography and the surface roughness of the films were analyzed by mechanical profilometer (Tencor P-7). The surface morphology of Al/Ni/TiO\(_2\) films was studied using (JEOL JSM 5800) scanning electron microscope (SEM) coupled with an energy dispersive X-ray analyzer (EDX) to study the chemical composition of the photocatalysts. The optical transmission spectra of the films were conducted with a UV–VIS JASCO V-770 spectrophotometer at a wavelength from 300-1500 nm.

### 2.4. Photocatalytic characterization

The photocatalytic experiments by exploiting sunlight irradiation were conducted on the 15\(^{th}\) of December 2020, under the conditions of the weather for that day (Biskra-Algeria). We intended to mention the date, as both the mean air temperature and relative humidity affect the solar radiation and therefore the photocatalytic efficiency of the films \[26-30\]. In addition, we aim for an in-depth study to compare the photocatalytic performance of TiO\(_2\) based thin films under sunlight irradiation every 15\(^{th}\) of each month.

In this study, Methylene blue (MB) dye has been chosen as a model of wastewater contaminants. Photocatalytic degradation of MB solutions by TiO\(_2\) based thin films was investigated under sunlight irradiation. The photocatalyst samples (20 cm\(^2\)) were dipped in 100 ml of MB solution (2ppm), in a Pyrex beaker at an angle of 36° ± 1 with tracking the direction of the sun manually during the experiments as an imitation of the solar panel system. Before the reaction, the photocatalyst was kept in the MB solution in the dark for 30 min to reach adsorption equilibrium, and then the irradiation tests were carried out from 8:30 am to 3:30 pm. During these experiments, the MB solution has stirred with a speed of 250 rpm.

### 3. Results & discussion

#### 3.1. TiO\(_2\) based thin films properties

Figure 1 shows the XRD patterns of Al/Ni/TiO\(_2\) thin films. The XRD pattern of pure TiO\(_2\) exhibits a tetragonal crystal structure with a single anatase phase (A) at the diffraction line 25.4° (JCPDS: 00-002-0387); this result is similar to a previous study \[31\]. The Ni-TiO\(_2\) film reveals that Ni doping TiO\(_2\) produced a change in the crystalline structure from anatase to anorthic structure of Ti\(_4\)O\(_7\) phase \[32\] with diffraction line 31.7° (JCPDS: 00-018-1402). The XRD result of Al-TiO\(_2\) thin film shows two peaks at 38.4
and 44.2 ° corresponding to the Ti$_3$O$_5$ (Monoclinic, JCPDS: 00-011-0217) and rutile (Tetragonal, JCPDS: 00-003-1122) phase, respectively. The Al-Ni-TiO$_2$ thin film reveals a similar XRD results to that of Ni-TiO$_2$ film. Rutile crystal phase has tighter band gap (3.0 eV) than that of anatase phase (3.4 eV) [33], therefore, it suggests low photocatalytic activity due to the recombination of electrons from the conduction to the valence band (hole). Crystal size, porosity, and roughness of TiO$_2$ material are ones of important factors influencing its catalytic activity. Choi et al. [34] disclosed that small crystal size is of importance for high photocatalytic activity of TiO$_2$ material. The primary crystal size was valued based on the effective crystal dimension $D$ computed using Scherrer equation which is given in the form

$$D = 0.9 \cdot \frac{\lambda}{B \cdot \cos \theta} \quad (1)$$

Where 0.9 is the Scherrer constant, $\lambda$ is the wavelength of X-ray (1.5406 Å), $B$ is the full wave half-maximum, and $\theta$ is the Bragg angle [35]. $D$ values were calculated for the most intense diffraction line (Table 1). The crystal size of TiO$_2$ based thin films was around 6-9 nm. Based on the literature [36, 37], Ni-TiO$_2$ catalyst promises high photocatalytic efficiency compared to other catalysts as it has small particle size (6.87 nm). Moreover, Ni and Al doping decrease the crystal size due to the incorporation of Ni$^{2+}$ and Al$^{3+}$ ions into cation sites of TiO$_2$ lattice.

![XRD patterns of TiO$_2$ based thin films.](image)

Fig. 1. XRD patterns of TiO$_2$ based thin films.
The 3D surface topography of un-doped TiO\textsubscript{2} and Al/Ni doped TiO\textsubscript{2} thin films is shown in Fig. 2. The root mean square (R\text{q}) surface roughness was calculated with the use of Apex analysis software (Table 1). The surface of TiO\textsubscript{2} thin film is heterogeneous with a height equal to 1890 nm. This surface is modified by the presence of Ni which makes the surface porous and flat with a certain difference in the density of pores dispersed randomly. Al doping TiO\textsubscript{2} films makes the surface homogenous. The height of Al/Ni/TiO\textsubscript{2} thin films is between 1.5-4.5 nm. R\text{q} values are in the range of 30-45 nm (Table 1). Ni-TiO\textsubscript{2} thin films suggest high photocatalytic efficiency for the discoloration of MB as it shows the high roughness value 44.5 nm [38]. Al-TiO\textsubscript{2} thin films have shown the lowest roughness 22.8 nm due to its homogenous surface.

Table 1. Summary of analytical data

| Parameters               | Units | TiO\textsubscript{2} | Ni/TiO\textsubscript{2} | Al/TiO\textsubscript{2} | Al/Ni/TiO\textsubscript{2} |
|--------------------------|-------|-----------------------|--------------------------|--------------------------|-----------------------------|
| Crystallographic Phase   | ---   | (A) Ti\textsubscript{4}O\textsubscript{7} | (R) Ti\textsubscript{4}O\textsubscript{7} |                       |
| Crystal Size             | nm    | 8.38                  | 6.87                     | 7.58                     | 6.97                        |
| Surface Roughness        | nm    | 30.7                  | 44.5                     | 22.8                     | 31.7                        |
| Film Thickness           | nm    | 316                   | 288                      | 284                      | 292                         |
| Transmission in Visible Range | %  | ~93                   | ~88                      | ~82                      | ~85                         |
| Optical Indirect Band Gap| eV    | 3.41                  | 3.35                     | 3.32                     | 3.26                        |
| Si Content               | wt%   | 35.8                  | 25.23                    | 19.27                    | 32.74                       |
| O Content                | wt%   | 59.06                 | 58.09                    | 58.00                    | 48.11                       |
| Ti Content               | wt%   | 11.14                 | 15.63                    | 20.88                    | 16.50                       |
| Ni Content               | wt%   | --                    | 1.06                     | --                       | 1.12                        |
| Al Content               | wt%   | --                    | --                       | 1.85                     | 1.53                        |
| photocatalytic efficiency| %     | ~84                   | ~93                      | ~64                      | ~86                         |
| Rate constant            | h\textsuperscript{-1} | 0.224                 | 0.428                    | 0.159                    | 0.320                       |
SEM images of TiO₂ based thin films show compact and uniform films as shown in Fig. 3. For Ni-TiO₂ thin films, it can be observed the presence of randomly distributed grains and pores which can increase the amount of MB adsorbed on these surfaces, and consequently, increasing the photocatalytic efficiency of the film. EDX analyses show a difference of the oxygen content in TiO₂ based thin films. The increase in oxygen content in thin films increases its transmittance and thus giving high band gap energy (Eg) value [33]. The O content in TiO₂ thin films is in the range 48-59 wt. % as shown in Fig. 3. Ni-TiO₂ thin film shows the higher value of O content (58.09 wt. %). Al/Ni doped TiO₂ thin films exhibits Ni and Al contents less than 2 wt. % (Table 1). The thickness (t) of TiO₂ based thin films was estimated by the gravimetric method using the relation...
Where \( t \) is the films thickness (cm), \( A \) is the surface area of the films (cm\(^2\)), \( M \) is the mass of the films (g), and \( g \) is the density of the film material (g.cm\(^{-3}\)) [39]. Table 1 shows that films thickness values confirm the 3D film growth as shown in Fig. 2. TiO\(_2\) films with the best high (1980 nm) and much high crystal size (8.38 nm) is the thickest film. The doping of TiO\(_2\) films by Ni and Al reduce the thickness of the films to 288 nm and 284 nm, respectively.

![Fig. 4. (a) UV-VIS optical transmission spectra of TiO\(_2\) based thin films, (b) Tauc plot for the optical band gap.](image)

Figure 4 shows the optical transmission spectra of the films and Tauc plot for the optical band gap (E\(_g\)). The transmission spectra show high transparency in the visible region for all the TiO\(_2\) based thin films. These films have a transmittance values greater than 80%. The highest transmittance value is for TiO\(_2\) pure with a high film thickness and oxygen content: 316 nm and 59.06 wt. %, respectively. It is tempting to conclude that the average transmittance is a function of film thickness and oxygen content with a proportional relationship (Table 1). The optical indirect band gap was estimated using Tauc and Menth method given by relation (eq. 3)

\[
(ahv)^{1/2} = C(hv - E_g)
\]

Where \( \alpha \) is the absorption coefficient (m\(^{-1}\)) (eq. 4), which should be identified by the equation 4, \( h \) is Planck’s constant (4.136*10\(^{-15}\) eV.s), \( v \) is Frequency of light (s\(^{-1}\)), \( C \) is a Constant, \( E_g \) is Optical indirect band gap (eV), \( t \) is the film thickness (m) and \( T \) is the optical transmittance (%) [40]. The band gaps of the films slightly decreased with doping TiO\(_2\) thin films by Ni and Al ions owing to the change in crystallographic phase from anatase to Ti\(_4\)O\(_7\) and rutile, respectively. In other hand, both degree of crystallinity [19], crystal size [17] and film thickness [39] are the of importance parameters controlling the film band gap value. Table 1 shows that the indirect band gap widens with increasing thickness [41]. The wide band gap (3.41 eV) for TiO\(_2\) thin film agrees with high crystal size (8.38 nm) and thickness (316 nm).
3.2. Photocatalytic performance

The photocatalytic performance of TiO$_2$ based thin films was evaluated through the photodegradation of MB in an aqueous solution under sun irradiation. Fig. 5(a) shows that MB decomposes continuously throughout the entire irradiation time for Ni-doped TiO$_2$ thin films. The rate of degradation varies according to the hour of irradiation, since solar radiation is affected by temperature, humidity, wind speed, etc. The photocatalytic efficiency ($\gamma$) is determined from the following equation [42]:

$$\gamma\% = \left(\frac{C_0 - C_t}{C_0}\right)$$

(5)

Where $C_0$ and $C_t$ are the concentrations of MB dye at times $t = 0$ and $t$, respectively. The photodegradation of MB can be fitted by a pseudo-first-order reaction kinetic model [43, 44]:

$$-\ln\left(\frac{C_0}{C_t}\right) = kt$$

(6)

Where $k$ is the pseudo first-order rate constant (h$^{-1}$) and $t$ is the irradiation time (hours). The degree of MB degradation was in the order Ni/TiO$_2$ > Al/Ni/TiO$_2$ > TiO$_2$ > Al/TiO$_2$ as shown in Fig. 5. Al/TiO$_2$ (rutile phase) film shows lower photocatalytic efficiency (~64%), than that of anatase (~84%) TiO$_2$ film (Table 1); it is well known that rutile phase has lower photocatalytic efficiency than anatase phase due to the low indirect band gap. Wang et al [45] studied the sonocatalytic degradation of methyl orange in the presence of nanometer anatase and rutile TiO$_2$ powders. The compared sonocatalytic activities showed that the catalytic activity of nanometer anatase TiO$_2$ powder is higher than that of nanometer rutile TiO$_2$ powder. Ni/TiO$_2$ (~93%), and Al/Ni/TiO$_2$ (~86%) as sun catalysts show an effective degradation rate compared to that of anatase TiO$_2$ catalyst due to the low crystal size, high roughness, and crystallographic phase (Ti$_4$O$_7$) (Table 1). Roughness enhancement increases surface area of the films [46], and consequently increases the quantity of adsorbed contaminant. Hence photodegradation predominates. In addition, the modification of TiO$_2$ films surface by Ni$^{2+}$ improves photocatalytic activity under sun light which can be attributed to the decreased recombination rate electron-hole pairs. As a transition metal, nickel metal is well known as it most often has remarkable catalytic properties and can form a wide variety of ionic species in a wide range of oxidation states which gives rise to variously colored complexes due to the different electronic transitions within the incomplete 3d$^8$ sub-shell. The doped metal plays an effective role in charge separation by capturing electrons. Begum et al. [47] discussed that Ni ions capture the electron that left a freer hole at the valence band which increases the holes concentration and leads to migrates to surface layer by withdrawing the electrons from the surface.

$K$ values were determined by regression analysis of lines slopes in Fig. 5(c). Table 1 shows $K$ values which increase with irradiation time for all TiO$_2$ based photocatalysts. Figure 5(d) shows that the discoloration rate constant is largest with Ni doped TiO$_2$ due to the low crystal size and high surface roughness. Al-TiO$_2$ (rutile) photocatalysts shows the smallest ($k$) value maybe owing to the high electron recombination rate. Eva et al. [33] reported that as rutile adsorbs OH$^-$ more effectively than anatase, the
amount of OH\(^-\) generated on TiO\(_2\) and diffusing to the bulk solution would be lower in rutile crystallites. This result leads to conclude that

![UV-vis spectra](image1)

![Degradation vs time](image2)

![ln(C/C\(_0\)) vs irradiation time](image3)

![Rate constant k](image4)

Fig. 5. (a) Variation of UV–vis spectra of MB during photodegradation over Ni/TiO\(_2\) thin films; (b) Plot of photocatalytic efficiency versus the degradation time; (c) plot of ln(C/C\(_0\)) versus irradiation time for TiO\(_2\) based films; (d) rate constant \(k\) of MB photodegradation.

the doping metal type on TiO\(_2\) photocatalysts is of most important effective parameter on the photodegradation of MB. As discussed in above, Ni doped TiO\(_2\) as transition metal increased the degree of photocatalysis under sunlight irradiation. In other hand, Al was chosen as non-transition metal (sub-shell: 3p\(^1\)), which decreased the photocatalytic activity of TiO\(_2\) thin films.

3.3. Effect of MB photodegradation process on the TiO\(_2\) based thin films properties

Figure 6 shows surface morphology and EDX analyses of TiO\(_2\) based thin films after photodegradation experiments under sunlight irradiation. It is clear to observe that the morphology of the samples is uniform and compact compared to that before photolysis experiments; maybe owing to the high photodegradation rates of MB dye that require high photocatalytic activity of the films which leads to erode of films outer coatings. These results suppose that the thickness and surface roughness of the films are decreased by the
Fig. 6. SEM and EDX analyses of TiO$_2$ based thin films after photodegradation process: (a) TiO$_2$ pure, (b) 3 wt. % Ni-TiO$_2$, (c) 3 wt. % Al-TiO$_2$, (d) 3 wt. % Al-3 wt. % Ni-TiO$_2$.

Photolysis process. Hence, it is suggesting that the reuse of these samples for second cycle of photolysis gives low photodegradation rate than the first one. EDX results show that the content of Ti and O decreased by the photocatalytic application of these films as shown in Fig. 6(b). Hoffmann et al. [24] reported that unless oxygen is supplied on a continuous basis to a photocatalytic reactor, the rate of photocatalytic oxidation will decrease dramatically after depletion of the primary electron acceptor due to charge-carrier recombination. Overall, Ti and O contents are decreased owing to the photocatalytic oxidation of MB on bulk-phase TiO$_2$. 
Fig. 7. Effect of photocatalysis process on oxygen content in the films.

Figure 7 shows the influence of photocatalysis process on oxygen content in the films. It is evident that the decrease in oxygen content is higher for Ni-TiO$_2$ films due to the high photodegradation rate as the O is the electron acceptor and the principal oxidant. The decrease in O content leads to the decreasing optical transmission.

Figure 8 shows UV-Vis transmittance spectra of TiO$_2$ based thin film samples and their indirect band gap after photolysis. Figure 8(a) indicates the interference fringes which imply that the films are relatively flat after sun photocatalysis experiments. Overall, the optical transmission of the films decreased with decreased films thickness by photodegradation process (Table 2). Kim et al. [48] found that the optical transmission is not exponentially related to the film thickness. This result suggests that the transmission of the TiO$_2$ based thin films is affected by other physical properties of the films. In this study, the transmission decreases is attributed to the decreased O content in the films by the sun photocatalysis process.

Fig. 8. (a) UV-VIS optical transmission spectra of TiO$_2$ based thin films after photodegradation process, (b) Tauc plot for the optical band gap.
Table 2. Effect of photocatalysis process on the TiO$_2$ based thin films properties

| Parameters               | Units | TiO$_2$ | Ni/TiO$_2$ | Al/TiO$_2$ | Al/Ni/TiO$_2$ |
|--------------------------|-------|---------|------------|------------|---------------|
| Film Thickness           | nm    | 223     | 252        | 281        | 265           |
| Transmission in Visible Range | %    | ~83     | ~80        | ~82        | ~82           |
| Optical Indirect Band Gap | eV   | 3.44    | 3.41       | 3.40       | 3.46          |
| Si Content               | wt%   | 52.40   | 47.52      | 52.44      | 49.95         |
| O Content                | wt%   | 40.30   | 37.87      | 41.37      | 40.87         |
| Ti Content               | wt%   | 7.30    | 13.00      | 4.93       | 7.52          |
| Ni Content               | wt%   | --      | 1.60       | --         | 0.20          |
| Al Content               | wt%   | --      | --         | 1.26       | 1.46          |

Table 2 shows an increase in band gap with varying values according to the photocatalytic activities of the samples. This increase may lead to the low electron transfer kinetics from the valence band to the conduction band driving photo-oxidation of contaminants when using these samples for a second cycle. Trapping electron-hole of wide band gap semiconductors require high energy for photocatalysis than that of tighter one. This result suggests that using the samples for a second photocatalytic cycle may give less photodegradation rate than the first cycle. Bansode et al. [49] reused the Fe doped TiO$_2$ thin films for three cycles as MB bleaching photocatalysts under UV light, and found that the nature of degradation remains unaltered.

4. Conclusion

This work focused on the effect of Ni and Al dopants as transition and non-transition metal respectively, on the photocatalytic performance of TiO$_2$ thin films synthesized via sol-gel dip-coating technique. The photocatalytic performance of TiO$_2$ based thin films were evaluated via the photodegradation of methylene blue under sunlight irradiation. Photocatalysis process show that grown phase, grain size, surface morphology and roughness, O content and indirect band gap are of importance parameters controlling the photocatalytic performance of TiO$_2$ based thin films. 3 wt. % Ni-TiO$_2$ photocatalysts show higher degradation rate (~93%) than the other deposits. The transition metal Ni dopant improves the physical and optical properties of TiO$_2$ thin films. Thus the photodegradation of MB predominates. The use of 3 wt. % Al as non-transition metal dopant impairs the photocatalytic activity of TiO$_2$ thin films under sunlight irradiation.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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