Influence of the number of layers and crystallization temperature on the photocatalytic activity of TiO$_2$ / In$_2$O$_3$ thin films

Abstract

The TiO$_2$/In$_2$O$_3$ thin films were prepared by the spin coating method, varying their number of layers (4, 8 and 16 layers). The Method of polymerization of complex (CPM) was used to synthesize the precursor resins in order to produce thin films. The TiO$_2$/In$_2$O$_3$ films were heat–treated at 300°C, 500°C and 700°C and characterized by X–ray diffraction, scanning electron microscopy (FEG–SEM), atomic force microscopy (AFM), UV–vis spectrophotometry and photoluminescence (PL). It was found that the band gap energy of the as–prepared TiO$_2$/In$_2$O$_3$ composite thin films decrease as temperature increases. According to the UV–vis diffuse reflectance spectra, the TiO$_2$/In$_2$O$_3$ composite shows good visible–light absorption ability. The photoluminescent properties of the films were studied at room temperature using a wavelength of 350nm excitation. High photoluminescent intensity was observed for the films treated at 300°C heat, studied in different films. The photocatalytic activity of the composite TiO$_2$/In$_2$O$_3$ was evaluated by the photodecomposition of methylene blue dye in aqueous solution and showed that all the composite samples presented excellent photocatalytic performance even when recycled. This study shows that the coupling of TiO$_2$ with In$_2$O$_3$ is an effective way to increase the TiO$_2$ absorption in the visible region for catalytic applications and that the temperature has a greater influence on the results than the number of layers.

Keywords: thin films, spin coating, TiO$_2$/In$_2$O$_3$, photocatalysis

Introduction

The semiconductor based in photocatalysis is considered as a promising technique for pollution treatment, due to its potential applications in environmental remediation and renewable energy generation, as well as the non–use products additional chemicals, and operating at room temperature.

TiO$_2$ is renowned as the most admirable material in photocatalytic applications, because of their high photocatalytic activities, low costs and nontoxic natures. However, due to their high Egap (3.2eV), they only absorb UV light. Much effort has been devoted to the further enhancement of the photocatalytic performance of TiO$_2$ for the degradation of various organic pollutants. A variety of materials, such as metal oxides and metal sulfides, have been coupled with TiO$_2$ to form composites. As one of the oxide semiconductor photocatalysts, In$_2$O$_3$, comparing with TiO$_2$, has the similar properties on photocatalytic activities. Meanwhile, In$_2$O$_3$ had proved to be an efficient sensitizer to extend the absorption spectra of oxide semiconductor photocatalysts from the UV region into the visible region, with a Egap of 2.8eV. However, the photocatalytic activity of pure In$_2$O$_3$ is very low due to the quick recombination of photogenerated electron–hole pairs. This material is obviously more suitable as a sensitizer to be combined with a large band–gap semiconductor. Since the conduction band energy level of In$_2$O$_3$ ($E_{CB} = -0.63$ eV) is more negative than that of TiO$_2$ ($E_{CB} = -0.5$ eV), the electron transfer from In$_2$O$_3$ to TiO$_2$ is possible.

Composite photo catalyst with two or more components can improve the separation of photo induced charges and enhance photocatalytic activity due to the high efficiency of the interfacial charge transfer between components. During the past decades, numerous studies have been successfully made to design different and efficient composite photocatalysts, such as noble–metal–based composites. Recently, a multilayer thin film of TiO$_2$/In$_2$O$_3$ has been used in solar cells, in order to improve the electrical properties of TiO$_2$ and increase the efficiency of the photovoltaic energy conversion, because the addition of In$_2$O$_3$ prevents the recombination of electrons / holes generated by the irradiation of TiO$_2$ particles, thereby increasing the formation of highly oxidative radicals on the TiO$_2$ surface, together with the visible absorption of In$_2$O$_3$ to 600nm. TiO$_2$ and In$_2$O$_3$ films have been studied by several investigators. However, TiO$_2$/In$_2$O$_3$ films are still understudied.

In this paper, we report the study of thin films of TiO$_2$/In$_2$O$_3$ composite prepared by method of polymerization of complex and deposited by spin coating. We also investigated the influence of the number of layers in the thin films of TiO$_2$/In$_2$O$_3$ on its photocatalytic efficiency and photoluminescent emission. The thin film was reused three times and shown to be efficient photocatalysts for degrading dyes. The photoluminescence emission shown that TiO$_2$/In$_2$O$_3$ composite was strongly affected by the crystallization temperature.

Experimental

Preparation of multilayer TiO$_2$/In$_2$O$_3$ thin films

The resin was prepared by the method of polymerization of complex, this method uses in situ polymerization, soluble metal polymerisation compounds are prepared with citric acid, and only...
then is added the polyalcohol, in this case ethylene glycol, which promotes the polymerization of metal compounds. As shown below: The thin film was obtained from a precursor solution using titanium (IV) isopropoxide and citric acid in a molar ratio of 3:1. Citric acid was added and dissolved in 100ml of distilled water under stirring at 70ºC. It was then slowly added the titanium isopropoxide until a homogeneous and transparent solution was obtained. Finally, ethylene glycol was added in a ratio of 40/60 (wt %) relative to citric acid and the temperature was raised to 90ºC. The same procedure was used to obtain the resin In2O3, substituting titanium isopropoxide by indium nitrate. The citric acid/metal cations (titanium isopropoxide, indium nitrate) at a ratio of 3:1 and ethylene glycol were added in a ratio of 40/60 (% by mass) relative to citric acid. The viscosity of the deposition resin was adjusted to 20mPa/s measured at room temperature.

The substrates were spin–coated by dropping a small amount of the polymeric resin onto them. Rotation speed and spin time were fixed at 700rpm for 3s and 7200rpm for 30s, using a commercial spinner (Chemat Technology KW–4B spin–coater). After deposition, the wet films were dried at 80ºC for 10min on hot plate. Four, eight and sixteen layers were deposited for each film and the procedure was repeated for each layer. The deposition of multilayer TiO2/In2O3 thin films (4, 8 and 16 layers) on substrates was illustrated in Figure 1. Finally, the films were heat–treated in the resistive furnace at 300, 500 and 700ºC for 2h. Two films were produced for each temperature and for each variation of the number of layers, to be characterized.

Results and discussion

X-ray powder diffraction patterns of TiO2/In2O3 films obtained by the spin–coating method and calcined at different temperatures and different numbers of layers deposited, as shown in Figure 2A–2D layers, (Figure 2B) 8 layers and (Figure 2C) 16 layers. The XRD characteristic peaks of anatase and In2O3 are clearly observed. The TiO2 phase was indexed according to the PDF No. 73–1764. The anatase oxide structure was confirmed by the diffraction peak of 2θ=25.3º. The In2O3 phase is confirmed by the diffraction peak of 2θ=30.3º. According to Poznyak,10 thin films of TiO2/In2O3 prepared with different crystallization temperatures did not reveal any additional phases. This indicates that no chemical interaction occurs from the TiO2 with In2O3. It is also observed that the increased temperature favors the increase in the intensity of the lines both for anatase and In2O3, which can be seen in (Figure 8).

The crystallite sizes of all synthesized thin films were estimated from the line broadening of the correlative X–ray diffraction peak of each crystalline phase, using the most intense peak of each phase (101) and (440) according to Scherrer’s equation.1,11 Chuanhao Li1 reports that the width of the peak of the anatase phase increases with the formation of the composite TiO2/In2O3, indicating a reduction of the crystal size, as can be seen in Table 1. It was observed that the crystallite size of the thin films increased as the calcination temperature increased. This increase resulted in increases in both particle growth and sintering.4

Yu et al.1,12 indicated that the addition of additives to titania had a suppressive effect on the crystal growth of TiO2 since the additives hindered the contact between TiO2 particles and inhibited crystallite growth during the heat treatment. Similar results have been reported in other TiO2 composite materials.13

The surface morphology, particle size and, surface roughness of the thin films were characterized by atomic force microscopy (AFM) as shown in Figure 3 and Figure 4. In the images it was observed that the surface of the thin films is composed by rounded morphology particles and these particles are evenly distributed on the surface of the film without cracks and pores. The average particle size of the films ranged from 15 to 33nm, which was estimated based on measurements of at
least 300 microspheres in the AFM images and by fitting the resulting distribution using a Gaussian function. Furthermore, the variations in particle size of all synthesized thin films were similar to the variation in the crystallite size calculated from the XRD patterns using the equation of Scherrer (Table 1). The average surface roughness of the films TiO$_2$/In$_2$O$_3$ crystallized at 500°C and 700°C are presented in Table 2. It was found that the increase of temperature increased the surface roughness. A larger film roughness value increases its specific surface, facilitating the contact of the adsorbed substances with existing crystals, thereby increasing its photocatalytic efficiency.

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Figure 2 X-ray diffraction pattern of the films TiO$_2$/In$_2$O$_3$ with (A) 4 layers, (B) 8 layers and (C) 16 layers, calcined at 300°C, 500°C and 700°C.

Table 1 Average of crystallite size for films TiO$_2$/In$_2$O$_3$ crystallized at different temperatures

| Samples                      | TiO$_2$      | In$_2$O$_3$ |
|------------------------------|--------------|-------------|
|                             | 500°C        | 700°C       | 500°C        | 700°C       |
| TiO$_2$/In$_2$O$_3$ (4 layers) | 12.96±0.049  | 14.15±0.233 | 11.57±0.176  | 20.00±0.021 |
| TiO$_2$/In$_2$O$_3$ (8 layers) | 12.62±0.459  | 29.31±0.452 | 10.64±0.480  | 19.37±0.035 |
| TiO$_2$/In$_2$O$_3$ (16 layers) | 11.45±0.077  | 22.98±0.042 | 14.04±0.091  | 16.17±0.190 |

The FE–SEM image exemplified in Figure 5 shows the cross section of the films TiO$_2$/In$_2$O$_3$ in the silicon substrate, varying the number of layers (4, 8 and 16) with heat–treated at 700°C. It can be observed that, the thickness of the thin films was 262.3, 593.3 and 708.3nm, respectively. Moreover, the FE–SEM image of the films of TiO$_2$/In$_2$O$_3$ exhibit high thickness uniformity, adhesion to the substrate and good densification.

Figure 3 Histogram distribution of particle size and image of the film surface TiO$_2$/In$_2$O$_3$ with (A) 4 layers, (B) 8 layers and (C) 16 layers, calcined 500°C.

Figure 4 Histogram distribution of particle size and image of the film surface TiO$_2$/In$_2$O$_3$ with (A) 4 layers, (B) 8 layers and (C) 16 layers, calcined 700°C.

The optical band gap energy (E$_{\text{gap}}$) was calculated by the Kubelka and Munk method, which is based on the transformation of diffuse reflectance measurements to estimate E$_{\text{gap}}$ values with good accuracy within the limits of the assumptions.\(^{14}\)

Thus, by the Kubelka and Munk method and plotting a term chart $F(R_s)\lambda^2$ as a function of the energy ($\hbar\nu$), one can get the value
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Figure 5 Morphology of the cross section of the film TiO$_2$/In$_2$O$_3$ crystallized 700°C, with (a) 4 layers, (b) 8 layers and (c) 16 layers.

Table 2 Roughness of the film TiO$_2$/In$_2$O$_3$ calcined at 500°C and 700°C

| N ° of Layers | Roughness(nm) | 500°C | 700°C |
|---------------|---------------|-------|-------|
| 4             | 1.43          | 1.48  |
| 8             | 0.73          | 1.23  |
| 16            | 0.93          | 0.93  |

Figure 6 show that an increase in the heat treatment produces a decrease in the Egap values. According to Jain et al., the observed decrease in band gap energy can be attributed to chemical composition, crystal structure, grain size and defects. Of all these contributing parameters, in this study the results observed in Figures 3, Figure 4 and Figure 6 shows that the optical properties of the films, such as the band gap, strongly depends on the size of the grain. The variation of the band gap with grain size due to quantum confinement has the quantitative form.

\[
E_{gap}^{nano} = E_{gap}^{bulk} + \frac{\hbar^2\pi^2}{2Mr^2}
\]  

(1)

Where ‘r’ is the radius of the nano–particle and ‘M’ is the effective mass of the system.

It is also known that the recombination time of the electron–hole pair in the TiO$_2$ semiconductor is small and that only radiation of wavelength less than 388nm (ultraviolet light) is sufficient to promote photoexcitation of the electrons from the valence band to the driving band. If there is a decrease in Egap between TiO$_2$ and In$_2$O$_3$ films, the transfer of photogenerated electrons to In$_2$O$_3$, which acts as an electron trap, occurs efficiently. In addition, the presence of In$_2$O$_3$ promotes a shift of the absorption edge of TiO$_2$ to the visible wavelength. This change in TiO$_2$ bandwidth energy for the UV region has been reported in the literature for TiO$_2$/In$_2$O$_3$ nanoparticles. It is within this context that it is believed that TiO$_2$/In$_2$O$_3$ films treated at 700°C present high technological potential to be applied in photocatalysis.

PL spectrum is a useful tool to investigate the fate of photogenerated electron and hole in a semiconductor, since PL emission results from the recombination of free charge carriers. Generally, a weaker PL intensity implies lower electron–hole recombination rate and corresponds to a higher photocatalytic activity.

Figure 7 illustrates the photoluminescence spectra (PL) of the films TiO$_2$/In$_2$O$_3$ calcined at 300, 500 and 700°C. All Samples were analyzed at room temperature with an excitation wavelength at 350nm. It was possible to observe a broad and intense emission band covering a large part of the visible spectrum (400–750nm).

The PL emission spectra show that an increase in temperature decreases the intensity of the photoluminescence that according to Pontes, as this property is associated with the structural disorder of the inorganic phase, the photoluminescent spectrum is more intense when the material is submitted for a longer time to the treatment Temperature (the carbon is eliminated without crystallization). This is a strong indication that the disordered phase (amorphous phase) is responsible for photoluminescence.

As the calcination temperature increases, the order begins to increase in the medium and long range, so the electron–hole transitions suffer a decrease, thus decreasing the intensity of the photoluminescent signal, and as a consequence a high photocatalytic activity.

The relative values of the variation in the concentration of methylene blue were used to study the degradation by UV radiation
of the TiO2/In2O3 thin films; the dye concentration as a function of irradiation time is shown in Figure 8 (I). During this process, it was observed that the concentration of methylene blue in the TiO2/In2O3 films decreases when exposed to UV radiation. The degradation efficiency of Methylene Blue was calculated using (Equation 1).

\[ \text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \]

where \( C_0 \) is the initial concentration and \( C_t \) is the concentration at time \( t \). In addition, \( A_0 \) is the initial absorbance and at is the absorbance after time \( t \) of the dye solution.

Furthermore, the film of TiO2/In2O3 calcined at 700°C shows a slightly higher degradation rate than the film of TiO2/In2O3 calcined at 300°C to 500°C; i.e., increasing the calcination temperature favors an increase the photocatalytic activity.

\[ D(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \]

(2)

Where \( C_0 \) is the initial concentration and \( C_t \) is the time concentration \( t \). In addition, \( A_0 \) is the initial absorbance and at is the absorbance after time \( t \) of the dye solution.

Figure 8 show the kinetic studies of the degradation of the thin films. All the catalysts followed first–order kinetics and the apparent rate constant was calculated by plotting \( \ln \left( \frac{C_0}{C_t} \right) \) versus time (Equation 3). The slope of the plot represents the apparent rate constant.22 The linear regression value obtained in this study was 0.98 and 0.99 (Table 3). According Sanoop, for all experimental results by linear regression of \( \ln (C/C_0) \) versus irradiation time, the value of \( R^2 \), larger than 0.95.

\[ \ln \left( \frac{C_0}{C_t} \right) = -k_t t \]

(3)

The recyclability of the TiO2/In2O3 sample was also investigated. The photocatalytic tests were performed using the same photocatalysts three times during each cycle of 350min and the results are compiled in Figure 9.

The photocatalytic process has been widely used in the treatment of domestic and industrial wastewater and the reuse of photocatalysts becomes very important, because it indicates the ability of the material to remain active even after use. It can see that the photocatalyst retains its efficiency even when reused after three reaction cycles, it can be said that there is not a considerable loss of mass during washing. Cycling uses, as well as, maintaining high photocatalytic activity are critical issues for long–term use in practical applications of the catalyst. Therefore, two criteria are required to be considered: (i) the stability of the catalyst to maintain its high activity over time, as
shown in Figure 9, and (ii) The ease with which the catalyst could be recycled from solution.19

**Table 3** Kinetics for MB photo-degradation by various TiO\(_2\)/In\(_2\)O\(_3\) multilayer films

| N\(^o\) Layers | Samples  | \(R^2\) | \(K(\text{min}^{-1})\) |
|----------------|----------|---------|-------------------------|
| 4              | Tiln300  | 0.99    | 0.0095                  |
|                | Tiln500  | 0.98    | 0.0138                  |
|                | Tiln700  | 0.99    | 0.0372                  |
| 8              | Tiln300  | 0.99    | 0.0253                  |
|                | Tiln500  | 0.99    | 0.0134                  |
|                | Tiln700  | 0.99    | 0.0223                  |
| 16             | Tiln300  | 0.98    | 0.0035                  |
|                | Tiln500  | 0.99    | 0.0211                  |
|                | Tiln700  | 0.98    | 0.023                   |

**Figure 9** Photocatalytic activity of the film TiO\(_2\)/In\(_2\)O\(_3\) with (I) 4 layers, (II) 8 layers and (III) 16 layers in different crystallization temperatures for the degradation of methylene blue dye with three cycles used. (A) 300°C, (B) 500°C, (C) 700°C.

**Conclusion**

TiO\(_2\)/In\(_2\)O\(_3\) composites have been prepared by the method of polymerization of complex and deposited by the spin coating method, varying the number of deposited layers and the calcination temperature. The obtained composites show a spherical morphology and high visible–light–harvesting capability. The TiO\(_2\)/In\(_2\)O\(_3\) thin films exhibit excellent photocatalytic performance toward the decomposition of the methylene blue. The photoluminescence of these films is strongly influenced by the temperature of crystallization; increased temperature decreases the intensity of photoluminescence. As the photoluminescence signal is the result of a combination of excited electrons and holes, the lower intensity indicates the decrease in the rate of recombination and thus the higher the photocatalytic activity. According to the obtained results, it was observed that the increase in the number of layers of TiO\(_2\)/In\(_2\)O\(_3\) films did not cause large changes in the results, unlike the crystallization temperature. The films were also recycled and reused to three cycles and shown to be efficient photocatalysts for degrading dyes.

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**Conflict of interest**

The author declares no conflict of interest.

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