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Optical Properties of Cobalt Doped TiO_2 Thin Films: Study of Degradation under Band Gap Edge of 412 nm Light Illumination

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Kobalt Katkılı TiO_2 İnce Filmlerin Optik Özellikleri: 412 nm Işık Aydınlatması Altında Bant Aralığı Sınırında Bozunmanın İncelenmesi

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Abstract

In this study, it has been aimed to investigate the effect of Co doping on the optical properties of TiO_2 thin film and the change in optical properties of Co doped TiO_2 thin film with the widest optical band gap during illuminating by light. For this purpose, Pure and cobalt-doped TiO_2 thin films have been prepared by sol-gel technique. The optical properties of the thin films have been characterized by ultraviolet-visible (UV-Vis) light spectrometer. The optical band gap, transmittance, reflectance and refractive index have been determined. The highest optical band gap has been recorded for the 3% Co doping as 3.01 eV. Additionally, it has been determined that since cobalt exhibits absorption characteristics that differ from TiO_2, particularly at longer wavelengths, it leads to a decrease in the effective refractive index for the composites. The results indicated that the cobalt additive significantly enhanced photo-degradation. To analyze this effect, the composite having 3% Co doping has also been illuminated by 412 nm light that corresponds to 3.01 eV between 20 minutes and 1 hour. As a result, a slight increase in the absorbance has been recorded.

***Keywords**: TiO_2 thin film; Sol-gel; Cobalt dopant; Photo-degredation.*

Öz

Bu çalışmada, Co katkısının TiO_2 ince filminin optik özellikleri üzerindeki etkisi ve en geniş optik bant aralığına sahip Co katkılı TiO_2 ince filminin ışıkla aydınlatılması sırasında optik özelliklerindeki değişimin incelenmesi amaçlanmıştır. Bu amaçla, saf ve kobalt katkılı TiO_2 ince filmler sol-jel tekniği ile hazırlanmıştır. İnce filmlerin optik özellikleri ultraviyole-görünür (UV-Vis) ışık spektrometresi ile karakterize edilmiştir. Optik bant aralığı, geçirgenlik, yansıma ve kırılma indisi belirlenmiştir. En yüksek optik bant aralığı %3 Co katkısı için 3.01 eV olarak hesaplanmıştır. Ayrıca, kobaltın özellikle uzun dalga boylarında TiO_2'den farklı soğurma özellikleri sergilemesi nedeniyle, bileşimlerin kırılma indisinde bir düşüşe yol açtığı belirlenmiştir. Sonuçlar, kobalt katkısının foto-bozunmayı önemli ölçüde artırdığını göstermiştir. Bu etkiyi analiz etmek için, %3 Co katkılı bileşimde 20 dakika ile 1 saat arasında 3,01 eV'a karşılık gelen 412 nm ışıkla aydınlatılmıştır. Sonuç olarak, absorbans değerinde nispeten bir artış görülmüştür.

***Anahtar Kelimeler:** TiO_2 ince film; Sol-Jel; Kobalt katkı; Foto-bozulma*

1. Introduction

In recent years, there has been significant interest in titanium dioxide-titania (TiO_2) materials due to their modified electronic and optical properties. These materials find extensive applications in areas such as photocatalysis (S.Scirè et al., 2021), photoelectrochemical solar cells (T.S. Bhat et al., 2021), bone implants (N. Sehrish et al.,2022) optical coatings (K. Albaidani et al., 2023) and sensors (E.A.S. Simonetti et al.,2021). In recent times, there has been a focus on studying bulk materials, nanoparticles, and thin films of TiO_2 doped with various elements to enhance their properties. Especially, the introduction of various transition metal ions into the TiO_2 lattice also induces varying strains and results in changes in the lattice parameters depending on the dopant concentration. This modification also enable to adjustment of the electronic, optic, and magnetic properties of the TiO_2 for various applications (M.Hamadanian et al. 2010, C.Stella et al. 2016).

The primary emphasis in these studies was on doping at Ti sites, with dopants such as Fe, Co, Cr, V, Ni, Cu, Mn, and Rb (J.R.Simpson and H.D.Drew 2004, G.He et al. 2008, P.C.McIntyre et al. 1997, Z.S.Cai et al.2011). Among these additives, due to the close values of atomic radii of cobalt (Co) and titanium (Ti), the seamless integration of Co atoms into the TiO_2 lattice is possible without inducing notable lattice distortions. This form of substitutional doping ensures a consistent dispersion of Co across the TiO_2 material, resulting in a uniform doping profile. Besides, as reported by (Yamada et al. 2011), it is known that ferromagnetism can be induced at room temperature with cobalt. On the other hand, it has been

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reported by Barakat et al. that the transition from the anastasis phase to the rutile phase for TiO_2 can be accelerated by the addition of cobalt (M.A. Barakat et al. 2005). It has been also reported by Tian et al. that cobalt doping to TiO_2 causes a change in the optical band gap (Jianjun Tian et al. 2012).

In the light of all this scientific literature, this study attempted to improve the optical properties of TiO_2 thin films with Co doping and also focused on the investigation of the photo-degradation properties of the sample with the widest optical band gap. In this context, the Co-doped TiO_2 thin film with the widest optical band gap has been exposed to light at the wavelength corresponding to its optical band gap for different time durations and the change of its optical properties has been discussed. Additionally, in the photo-degradation analysis, the Co-doped TiO_2 thin film as well as the Ruthenium -coated Co-doped TiO_2 thin film have also been taken into account.

2. Experimental

2.1 Materials

Titanium-4-isopropoxide (TTIP) used in the preparation of Co-doped TiO_2 films has been obtained from Sigma Aldrich Company with CAS number of 546-68-9. Methanol (CH3OH) and acetic acid (CH_3COOH) have been supplied from Sigma Aldrich Company with the CAS numbers of 67-56-1 and 64-19-7, respectively. Additionally, cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) has been purchased from Acros Organics Company with the CAS number of 7791-13-1. The alcohols used for cleaning purposes are of technical quality and have been supplied by the Shell Company. The microscope slides (soda lime glass) substrates have been purchased from IsoLab Company with 50 pieces.

2.2 Preparation of Co-doped TiO_2 Thin Films

TiO_2 doped with cobalt in 1%, 2%, 3%, 4%, and 5% concentrations have been synthesized by sol-gel method at room temperature. The preparation steps of the samples in thin film form onto glass substrates have been illustrated representatively in Figure 1. Glass has been used as the substrate to be coated with films. The glasses have been cleaned ultrasonically in DI-W (deionized water) for 15 minutes, then ultrasonically cleaned in isopropyl alcohol for 15 minutes, rinsed with DI-W and dried. After mixing 3.5 mL of Titanium-4-isopropoxide with 31.5 mL of methanol in a magnetic stirrer for 1 hour, 350 μL HCl has been added and this mixture has been stirred in a magnetic stirrer for 24 hours to obtain a homogeneous mixture (TiO_2 solution). $CoCl_2.6H_2O$ has been used as the starting material for the cobalt additive. A cobalt solution has been prepared by dissolving 0.2M $CoCl_2.6H_2O$ in the appropriate volume of methanol. This solution has been added into the previously prepared TiO_2 solution at the rate of 1, 2, 3, 4, and 5% by volume of the cobalt sol solution and mixed. Un-doped (i.e. pure) TiO_2 and 1, 2, 3, 4, and 5% (V/V) Co-doped TiO_2 solutions have been coated on previously prepared substrates by spin coating method at 3000 rpm in 30 seconds. To evaporate the solution, the obtained films have been heated at 100 °C for 10 minutes. Finally, the films have been annealed at 500°C for 30 minutes.

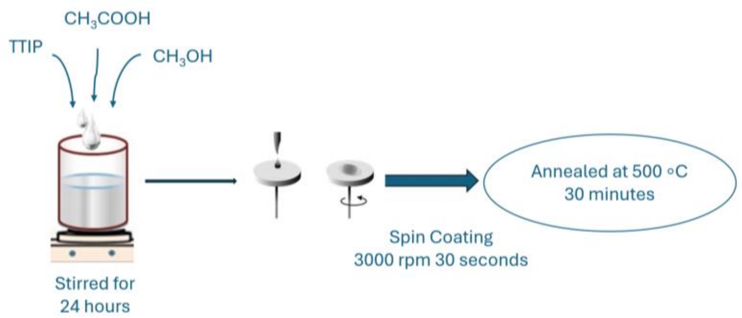

Figure 1. The preparation steps of the samples prepared onto glass substrates.

2.3 Methods

The structural analysis of the TiO_2 has been determined by X-Ray Diffraction (XRD) patterns obtained by PANalytical X'Pert PRO XRD model XRD device between 2θ=15°-70°. A CuK_α source with the wavelength of 1.54059 Å has been in an XRD device. The scanning rate was 1°/min. The surface morphology of the thin film has also been viewed by images taken from Zeiss EVO LS 10 model Scanning Electron microscope (SEM). The optical properties of the samples have been determined by using their UV-Vis spectra obtained from Perkin Elmer Lambda 35 UV/Vis spectrometer at room temperature between 350-1100 nm wavelength.

3. Results and Discussions

3.1. Structure, Morphology and FTIR Analysis

As shown in Figure 2, pure TiO_2 thin film exhibits a broad diffraction peak from 2θ = 20° to 70°. These peaks corresponding to 26.35°, 37.58°, 48.40°, 55.45° and 59.35° is attributed to (101), (004), (200), (105) and (211) planes, respectively, for the anatase phase. These XRD peaks are consistent with the characteristic XRD peaks of TiO_2 thin films (JCPDS Card No. 21-1272) (V. Mishra et al. 2019, F. Z. Haque et al. 2016, N.A. Bakr et al. 2017).

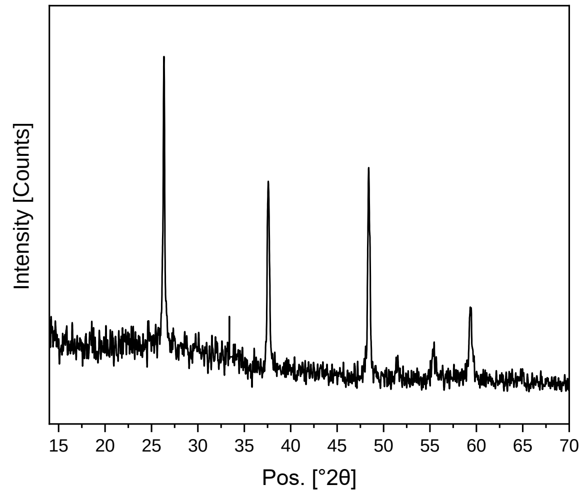

Figure 2. XRD patterns of the pure TiO_2.

Figure 3 shows an SEM image of the surface of a pure TiO_2 thin film at 50,000x magnification. The image reveals the formation of inhomogeneous particles with various geometries.

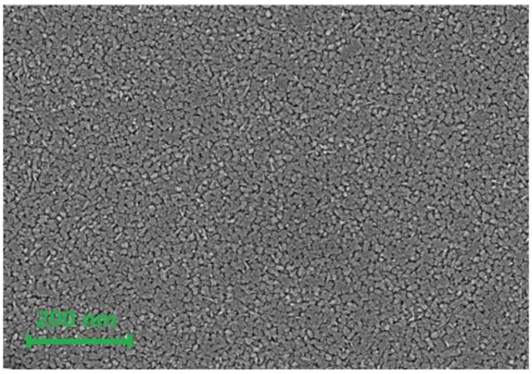

Figure 3. SEM image of the pure TiO_2.

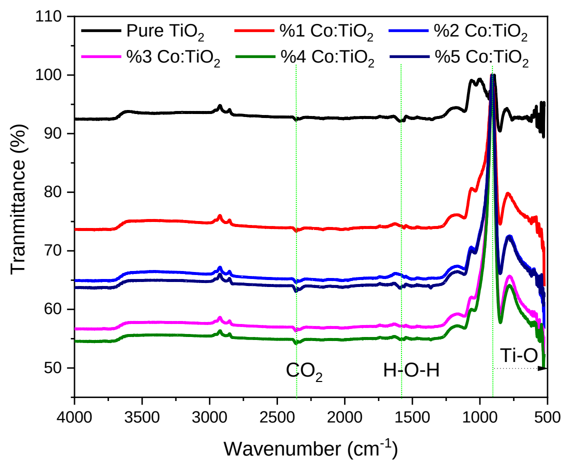

Figure 4. FTIR Spectrum of the pure and Co doped TiO_2 samples.

Fourier Transformed Infrared (FTIR) spectroscopy has also been employed to investigate the TiO_2 lattice vibrations significantly influenced by the presence of Co atoms. Figure 4 displays the FTIR spectra of pure and Co-doped TiO_2 thin films. The wide band observed between 500 cm^{-1} and 900 cm^{-1} is associated with anatase titania, and it is attributed to the Ti–O stretching and Ti–O–Ti bridging stretching modes (P. Praveen et al.,2014, C. Stella et al.,2016). In pure TiO_2, the Ti–O frequency peak has been observed at 553 and 765 cm^{-1}, while in the Co doped TiO_2 samples, the shift in this peak indicates the presence of oxygen vacancies and confirms the formation of Co–O bonds due to the substitution of Co atoms in the TiO_2 lattice. Additionally, compared to the pure sample, the doped samples show shifts towards higher wave numbers, suggesting the successful doping of Co atoms into the TiO_2 lattice (B. and A. Choudhury ,2012, K. Das et al., 2009). The peak at 1035 cm^{-1} is also attributed to Si-O-Si vibrations, likely originating from the soda-lime glass substrate (J. Wan et al., 2021). The peak at 1580 cm^{-1} corresponds to the bending vibration mode of physisorbed water molecules (H–O–H) on the sample surface (M. Hamadanian et al.,2010). Additionally, the bands at 2351 cm^{-1} and 2800 cm^{-1} confirm the presence of respectively CO_2 molecules and C-H, detectable due to the measurement being conducted in air. Finally, the peak appeared between 3200 cm^{-1} and 3400 cm^{-1} is associated with the O–H stretching vibration of the hydroxyl group (M. Hamadanian et al.,2010).

3.2 Analyzes of Optical Parameters of Samples Depending on Their Interaction with UV-Vis Light

The UV-Vis spectroscopy technique has been realized to determine the photo-activated optical features of the pure TiO_2 and TiO_2:Co thin films. The UV-Vis light absorption spectra of the samples have been shown in Figure 5(a).

As shown in Figure 5(a), the pure TiO_2 film shows typical absorption in the UV range and the optical absorption of the pure TiO_2 decreases considerably from the UV to near IR region of the electromagnetic spectrum. The same behavior with increasing wavelengths of light has been observed for the Co:TiO_2 thin films. However, the absorbance values of the Co-doped TiO_2 thin films are less than that of pure TiO_2 between the wavelength of 350 nm and 550 nm. As a result of Cobalt substitution for titanium in the TiO_2 lattice can modify the band gap of the material. The electronic structure changes associated with Co incorporation could result in a shift of the absorption edge to longer wavelengths, leading to a decrease in absorption in the specified range. Additionally, the introduction of cobalt ions into Ti sites may lead to crystal field effects. The local environment around the Co ions can influence the energy levels of the transition metal d orbitals, impacting the electronic transitions and, consequently, the absorption spectrum. Moreover, cobalt incorporation could induce local structural distortions around the substituted sites. These distortions may alter the electronic and optical properties of the TiO_2 lattice, contributing to changes in absorption characteristics.

To evaluate the effect of Co contribution to TiO_2 on the band gap, the direct allowed transition energy band gap values of the pure TiO_2 and the Co:TiO_2 have been determined by using the $(\alpha h\nu)^2=f(h\nu)$ Tauc's plots given in Figure 5(b). The direct optical band gap (E_g) has been calculated by Eq. (1):

$$(\alpha h\nu)^2 = A\left[E - E_g\right] \qquad (1)$$

where α is the absorption coefficient, $E=h\nu$ represents the energy of incoming photon, and A is the coefficient of proportionality. The estimated direct optical band gap value of the samples has also been listed in Figure 5(b). As shown in Figure 5(b), The E_g values of all Co-doped samples are greater than the E_g value of pure TiO_2 thin film, and the highest band gap value has been recorded as 3.01 eV at the value of 3% Co doping.

The increase in the calculated optical band gap suggests a modification of the electronic band structure of the TiO_2:Co thin films. This modification could be due to the introduction of Co atoms into Ti sites, leading to changes in the energy levels and electronic transitions. On the other hand, the fluctuation in the optical band gap implies many factors may co-operate on the optical band gap (Jianjun Tian et al. 2012). According to Toyosaki et al. (H. Toyosaki et al.,2005) and Hirose et al. (Y. Hirose et al., 2006) when Ti site is substituted by Co, this can increase the optical band gap. In the increase in the optical band gap may also be attributed to the relevant substitution. Furthermore, as was reported the increase in E_g may be related to the enhancement of compressive stress due to Co doping. The possibility of occurrence of increased compressive stress had already been mentioned by Shi et al. (J. Y. Shi et al.,2006).

According to Shi et al., this could be attributed to the larger ionic radius of Co^{2+} (65 pm) compared to Ti^{4+} (60.5 pm), which creates a variable octahedral ligand field in TiO_2. Consequently, the stress resulting from lattice distortion contributes to an increase in Fermi energy and the energy of the lower edge of the conduction band (J. Y. Shi et al., 2006). Moreover, the slight decrease in absorption accompanying increasing band gap may indicate some changes in charge carier dynamics. The addition of Co might be affecting the efficiency of charge separation and migration, leading to a reduction in the number of electrons available for absorption. Furthermore, the higher band gap can be the result in a decrease in the generation of electron-hole pairs upon exposure to light. This may be attributed to changes in the electronic structure that affect the photoexcitation process in the Co:TiO_2 samples. When evaluated in terms of technological applications, the increase in the band gap value of TiO_2 due to Co doping can make TiO_2 more suitable for applications requiring UV detection.

This is important in fields such as UV sensing, imaging, and monitoring, where the ability to detect ultraviolet light is essential. Moreover, TiO_2 with an increased band gap can be used in protective coatings and films that can block harmful UV radiation while allowing visible light to pass through.

To determine the influence of Co doping on the refractive index (n) of the pure TiO_2 thin film, the transmittance and reflectance spectra of the samples shown in Figure 6(a) and (b), respectively have also been examined. While the transmittance (T) and absorbance (A) values of the samples have been measured with UV-Vis spectrometer.

Reflectance values have been calculated according to Eq. (2):

$$R = 1 - A - T \qquad (2)$$

While all other Co-doped thin films, except 4% Co-doped TiO_2, have higher transmittance values than pure TiO_2 in the 350-700 nm wavelength range; it has lower transmittance values at wavelengths larger than 700 nm. However, higher transmittance was observed in the 4% Co doped sample than pure TiO_2 in the entire wavelength range studied. Based on this point, it can be thought that 4% Co contribution is the most suitable concentration for better transparency for TiO_2 compared to other additives. On the other hand, except for 4% Co doping, the decrease in transmittance values and increase in absorbance values of TiO_2 thin film in the 700-1100 nm range with Co doping can be attributed to the increased optical density in the crystal lattice with the doping. Namely, the presence of Co ions in the TiO_2 lattice may increase the optical density of the material, particularly in the near-IR region. This increased optical density can result in higher absorption and lower transmittance. Additionally, the transmittance values of all samples tended to increase when changing from the UV region to the near-IR region.

Considering the reflectance changes given in Figure 6(b), while the 1% Co-doped sample received reflectance values almost close to pure TiO_2 in the 350-700 nm range; with increasing Co contribution, lower reflectance values were recorded in the same wavelength range compared to the pure TiO_2. At lower Co concentrations (1% doping), the influence of Co on the band structure of TiO_2 can be minimal, resulting in reflectance values similar to pure TiO_2.

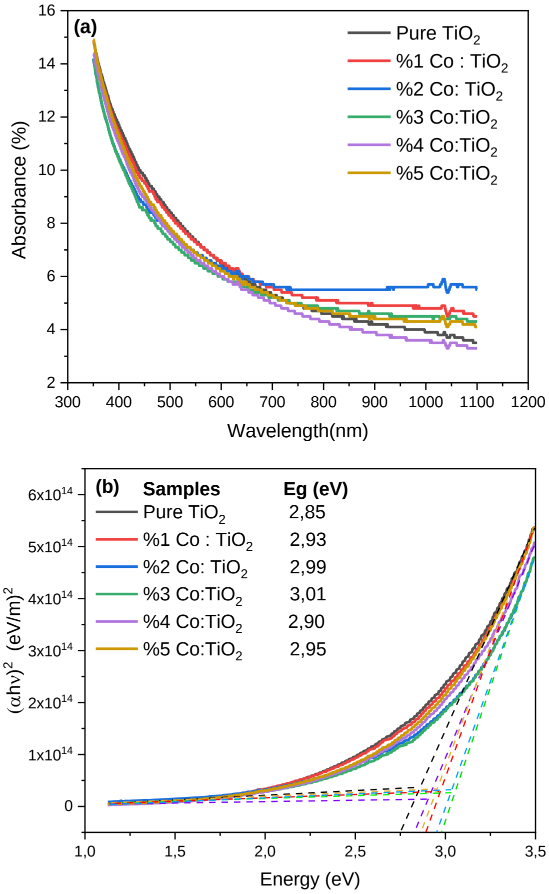

Figure 5 (a). UV-Vis light absorption spectra and **(b)** versus Energy curves of the samples

As Co concentration increases, the change of the band structure can become more important, leading to changes in optical properties and lower reflectance. When shifting to the near-IR region, reflectance values continued to decrease with increasing wavelength for all samples; however, except for the 4% Co added sample, the reflectance values for the other samples were higher than the pure TiO_2. The decrease in reflectance values in the near-infrared (NIR) region for most samples, except the 4% Co-doped sample, may be related to the introduction of energy levels by Co dopants that enhance NIR transparency.

By using reflectance values (*R*), the refractive index of the samples has been calculated by Eq. (3) (Thombare J.V. et al. 2013, Lohar G.M. et al. 2014).

$$n = \frac{1 + R + \sqrt{R}}{1 - R} \quad (3)$$

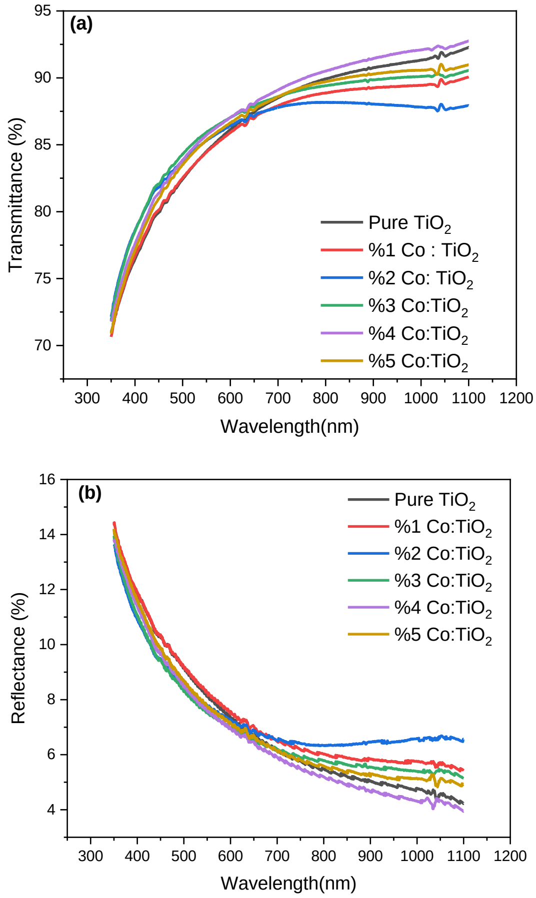

Figure 6. UV-Vis light **(a)** transmission and **(b)** reflectance spectra of the samples.

As shown in Figure 7, due to the Co contribution to the TiO_2, refractive indices higher than those of the pure TiO_2 film have been experimentally determined for light up to 500 nm wavelength. However, when the incident light is 800 nm and above, the refractive indexes for Co contributions excluding the 4% Co contribution, have been determined to be lower than the value of pure TiO_2. This behavior can be explained by the fact that the presence of cobalt could induce structural changes in the TiO_2 lattice, affecting its optical properties differently at various wavelengths. These changes may result in a wavelength-dependent refractive index behavior. Additionally, since cobalt may exhibit absorption characteristics that differ from TiO_2, particularly at longer wavelengths, this absorption could lead to a reduction in the effective refractive index.

3.3. Photo-degradation Properties of the 3% Co-doped TiO_2 thin films with Ruthenium dye coating under 412 nm Light Illumination

In the first part of the experimental study, the widest optical band gap was detected as 3.01 eV in the Co:TiO_2 thin film samples with 3% Co doping. Starting from this point, the second part of the experimental study is devoted to examining the optical properties of 3% Co:TiO_2

thin film by photo-degradation. For photo-degradation, the relevant sample has been aged by light with a wavelength of 412 nm, which corresponds to the bad gap energy of the sample, for a period ranging from 20 minutes to 1 hour.

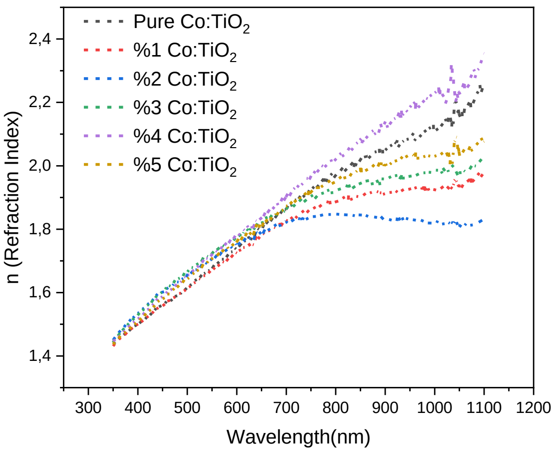

Figure 7. The variations of refractive index of the samples with wavelength.

For comparison, photo-degradation processes have been carried out for three different samples: glass coated with ruthenium dye as a thin film (coded as RD), glass coated with 3% Co:TiO₂ thin film (coded as 3% Co:TiO₂), and glass coated with ruthenium dye on 3% Co:TiO₂ thin film (coded as 3% Co:TiO₂/RD). Then the absorbance and transmittance spectra of the samples aged with 412 nm light for 20, 30, 40, and 60 minutes have been measured between 350-1100 nm wavelength range by UV-Vis spectrometer. The absorbance spectra of the three samples aged with 412 nm light for 20, 30, 40, and 60 minutes along with non-aged ones have been shown in the panels of Figure 8.

As shown in Figure 8(a), before the ruthenium dye-coated glass is illuminated with 412 nm light, it has two absorption peaks in the absorbance spectrum, one centered at 390 nm and the other centered at 540 nm. The absorption bands observed at 390 nm and 540 nm can be attributed to a metal-to-ligand charge transfer (Abdulraheem S. A. Almalki et al. 2021, Puhong Wen et al. 2012).

On the other hand, it has been determined that the center of the absorbance peaks did not change in the absorbance spectrum obtained after illumination with 412 nm light for 20 minutes. Still, the absorbance intensity increased for both peaks (see Figure 8(a)).

The transmittance spectra of the three samples aged with 412 nm light for 20, 30, 40, and 60 minutes along with non-aged ones have been shown in the panels of Figure 9. As shown in Figure 9(a), before the ruthenium dye-coated glass is illuminated with 412 nm light, the transmittance spectrum has two troughs, one at 390 nm and the other at 540 nm, due to charge transfer. After 20 minutes of illumination, the transmittance slightly decreases across the entire wavelength range, indicating easier electron excitation. Figure 9(c) demonstrates that the transmittance of the 3% Co-doped TiO2/RD thin films rises when exposed to 412 nm light, in contrast to the films that remain unexposed.

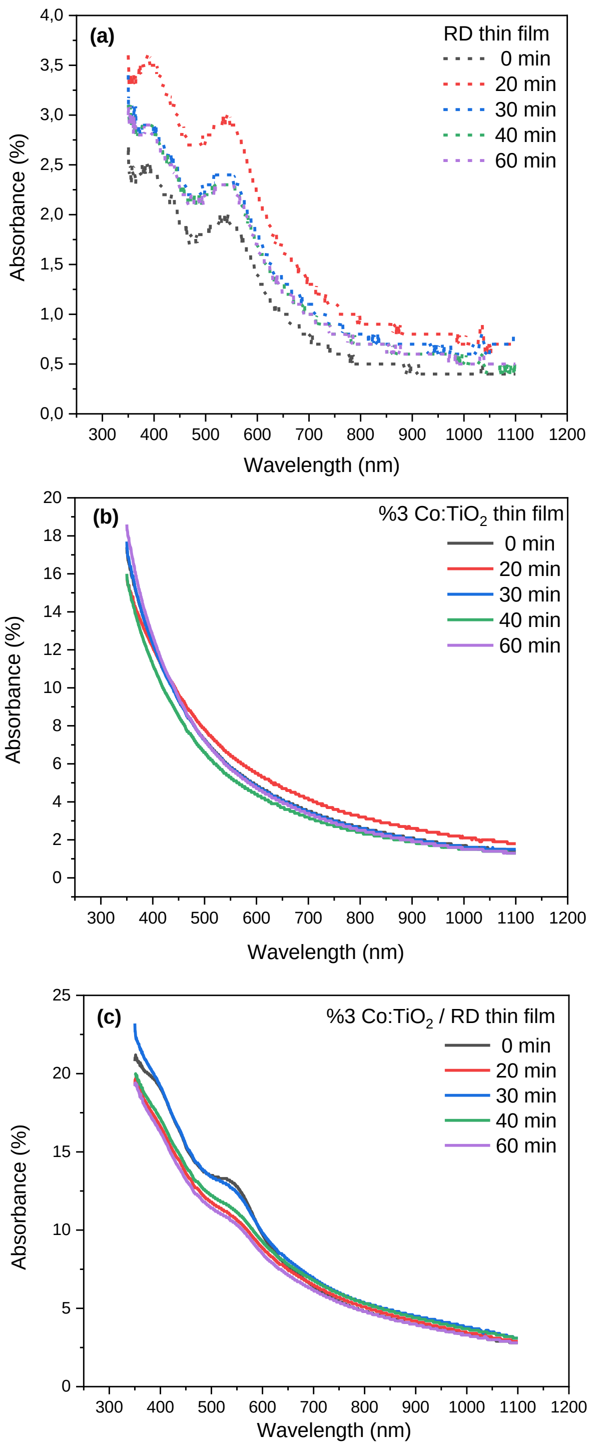

Figure 8. The variations of absorbance spectra of the samples (a) RD thin film (b) %3 Co:TiO₂ thin film (c) %3 Co:TiO₂/RD thin film under 412 nm light illumination at different time durations.

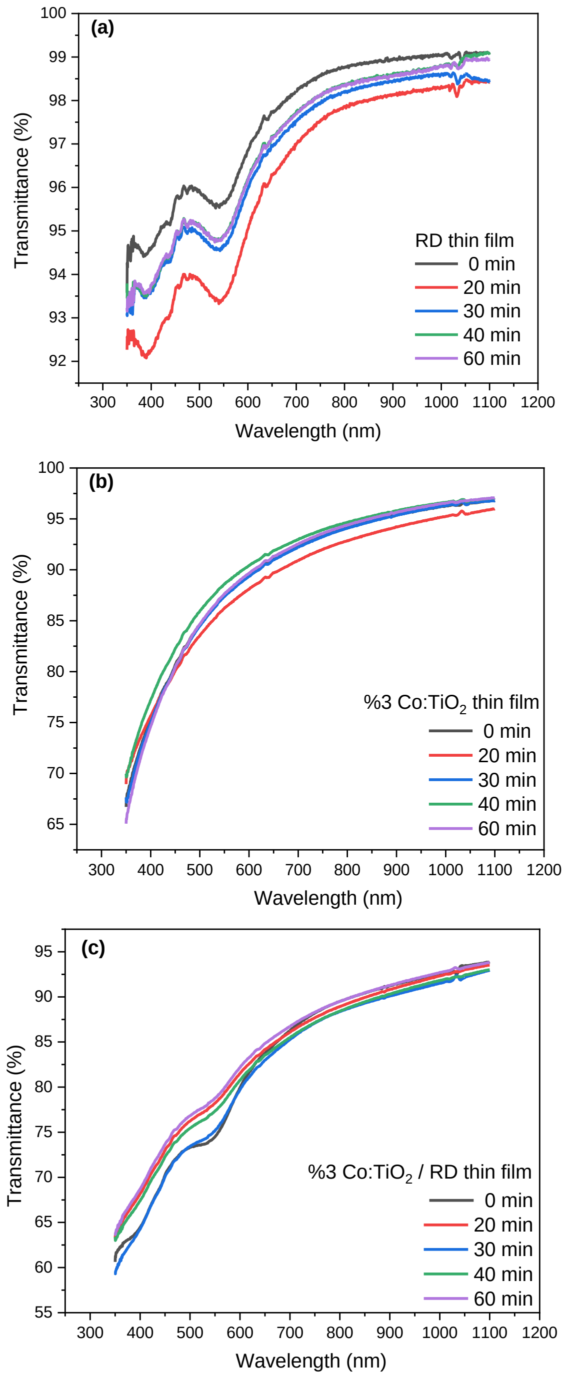

Figure 9. The variations of transmittance spectra of the samples (a) RD thin film (b) %3 Co:TiO_2 thin film (c) %3 Co:TiO_2/RD thin film under 412 nm light illumination at different time durations.

4.Conclusions

Pure and cobalt-doped TiO_2 thin films have been synthesized by using the sol-gel method at room temperature.

The increase in absorbance values means that electrons are excited more easily after illuminating the film with 412 nm light. Considering the absorbance spectrum of 3% Co:TiO_2 coated thin films on glass given in Figure 8(b), it has been observed that the absorbance increased slightly in the entire measured wavelength range after 20 minutes of light illumination. Figure 8(c) clearly shows that the absorption values of the 3% Co-doped TiO_2/RD thin films decrease in the range of 390 nm to 540 nm compared to both the films that were not exposed to light and those exposed to 412 nm light.

The synthesis involved the acid hydrolysis of TTIP and cobalt chloride, with cobalt concentrations varying at 1%, 2%, 3%, 4%, and 5%. It has been shown that pure TiO_2 thin films crystallize in the anatase phase and granules of different geometries are formed on the film surface. The optical parameters of the pure and cobalt-doped TiO_2 thin films have been characterized by UV-Vis spectroscopy. The study demonstrated that as the concentration of cobalt dopant increased, the absorption, transmission, and reflection of the TiO_2 thin films also changed. Moreover, an increase in cobalt concentration led to a reduction in the band gap. All thin films showed increased transmittance when moving from the UV to the NIR region. The results indicated that the cobalt additive significantly enhanced photo-degradation. To optimize this effect, thin films have been exposed to 412 nm light, matching the band gap edge, for durations between 20 minutes and 1 hour. It has been observed that the positions of absorbance peaks remained stable in the spectrum, while a slight increase in absorbance occurred after 20 minutes of illumination at 412 nm.

Declaration of Ethical Standards

The authors declare that they comply with all ethical standards.

Credit Authorship Contribution Statement

Author-1: Experimental Design, Investigation, Methodology and Experiment, Writing – original draft, Verification, Visualization Analysis, Review and Editing – original draft, References.

Author-2: Experiment, Writing – original draft, Visualization, Writing – original draft, References.

Author-3: Investigation, Project Management, Visualization, Writing – original draft, Review and Editing – original draft, References.

Declaration of Competing Interest

The authors have no conflicts of interest to declare regarding the content of this article.

Data Availability

All data generated or analyzed during this study are included in this published article.

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