Influence of Cadmium Doping on Structural, Optical, electrical and Photocatalytic properties of TiO_2 Thin Films Prepared by Spray Pyrolysis Technique

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Abstract

Undoped and doped cadmuim titanium oxide thin films at different percentage (1, 3, 4, and 5) % were fabricated by spray pyrolysis by using a solution of titanium tetrachloride and ethyl alcohol. The films have been deposited on heated quartz substrates at 623 K. After annealing for 120 min at 823 K, the initially amorphous films became polycrystalline with a predominant anatase structure and average crystallite sizes depending on dopant Cd concentration. Atomic force microscope (AFM) results show that the addition of the Cd to TiO_2 thin films become smooth. Optical study shows the optical band gap, and transmission has been increasing with increasing doping concentration in TiO_2 thin films. The electrical resistivity is decreases with increasing doping concentration Cd in TiO_2 thin films could be attributed to the increasing charge concentration. Photocatalytic activity of the TiO_2 films were studied by monitoring the degradation of aqueous methylene blue under UV light irradiation and was observed that increasing doping concentration had good photocatalytic activity which was explained as due to the structural and morphological properties of the films.

Keywords: TiO_2, Spray Pyrolysis, cadmium dopent, Structural Properties, Optical Properties, and photocatalytic properties**.**

1. Introduction

Over the last few years a great attention has been focused on the titanium dioxide (TiO_2) thin films because its excellent materials in many applications, such as in the field of sensors, antireflection coatings, gas sensors[1], solar cells[2]and photocatalysis[3,4]. By doping, especially

with transition metal atoms, these properties can be improved as desired, while keeping the films chemical and mechanical stability [1].

There are many methods that can be used to prepare TiO_2 thin films with desired properties including sol–gel[4-7], sputtering[8], anodic oxidation[9-14], pulsed laser deposition (PLD)[15], and spray pyrolysis[1-3,16-18]. Of all the afore-mentioned thin film fabrication methods, spray pyrolysis is widely used because of its simplicity, cheap chemical deposition procedure, allowing the growth of rough-surface films at atmospheric pressure, on large area. By this method, dopants can be easily introduced into the matrix of the film by using appropriate precursors [1, 16].

In this paper we have investigated the effect of cadmium doping on structure, optical , electrical and photocatalytic properties of TiO_2 thin films prepared by spray pyrolysis.

2. Experimental work

Undoped and cadmium-doped titanium oxide thin films were deposited on heated quartz substrate (623 K), by spraying an appropriate solution from a sprayer, placed at 30 cm in front of the heated substrate holder.

The starting solution was prepared by using (2 ml) titanium tetrachloride ($TiCl_4$, purity 99.9%, 1.726g/cm3 density) which is made in "England" dissolved in (20 ml) ethyl alcohol (96%). Filtered air was used as a carrier gas, the deposition time was set to 5 sec, the (undoped and doped) samples were annealed at 823 K in air for 120 min. Salt[$CdCl_2.6H_2O$] are used to dope TiO_2 films for different percentages (1,3,4 and 5%) of dopant.

The structural properties of the prepared films were studied by X-ray diffraction measurements (Philips PW 1050 X-ray diffractometer, with CuKα radiation (λ= 1.54059 Å)). The morphology of the films was studied by Scanning Electron Microscopy (SEM) type VEGA TE SCAN equipment operated at 30 keV. AFM studies were performed using a scanning probe microscopy (CSPM-5000). After annealing in the air the electrodes were deposited onto film surface by thermal evaporation of aluminum in vacuum system. The Edward E 306A coating system was used for this purpose, under pressure of about 10^{-5} torr. The best condition for good ohmic contact was satisfied by a layer of 200 nm. To study the electrical characterization of the TiO_2 films, electrical resistivity measurements were performed using two point probe method. The current measurements carried out by applying voltage supplied to the sample from a

stabilized d.c. fine power supply, type L 30 – 2 Farnell of range (0.1 – 5)V. The current passing through the sample was measured using a Keithley (602) electrometer.

Ellipsometer equipped with a He-Ne laser source (λ= 632.8 nm) were conducted to calculate film thickness. UV- VIS Spectrophotometer was used to measure the transmittance of TiO_2 films within the wavelength range of (300- 1100 nm). Using the optical transmittance spectra, the absorption coefficient and the band gap of TiO_2 were evaluated.

The photocatalytic activity of TiO_2 films was evaluated from the degradation of methylene blue (MB) during its catalytic decomposition. The MB ($C_{16}H_{18}C_lN_3S$) is an organic water soluble cationic dye found in waste waters and is potentially toxic. An aqueous solution of MB (100 mg/l) was taken in the reactor and was constantly stirred. The pH of the solution was adjusted to 3 with dilute hydraulic acid was added. The quartize slide coated with TiO_2 film of area 4.5 cm^2 was immersed in to the MB solution. Initially the MB solution with TiO_2 film was kept in dark for 30 min to establish adsorption–desorption equilibrium. After this stabilization period the TiO_2 film was irradiated with ultraviolet (UV) light source with central wavelength emission at 365 nm. The absorbance of the MB solution was monitored at intervals of 30 min using a UV–Vis spectrophotometer. The rate of photodegradation of MB solution in the case of each film was analyzed by monitoring the intensity variation of the main absorption band of MB at 605 nm.

3. Result and Discussion

3.1. X-Ray Diffraction study

The crystal structure of TiO_2 films was investigated through X-ray diffraction (XRD). The X-ray diffraction spectrum of pure and doping TiO_2 films with cadmium for different doping concentration (1,2,3,4 and 5) % deposited on quartz substrate at annealing temperature(823 K) for (120min) are shown in Fig. (1). It is found that all the films are polycrystalline with a tetragonal crystal structure. All films show diffraction peaks belong to anatase A(101). The diffraction peaks are in good agreement with those given in JCPD data card (JCPDS no .21-1272) for anatase phase. It is observed that the pure TiO_2 films exhibit a polycrystalline having (101), (004) and (200) planes of high peak intensities. The doped titanium oxide films become less crystalline than undoped sample. The crystal size was calculated from the full width at half

maximum (FWHM) (β) of the preferential orientation diffraction peak by using the Scherrer equation [16]

$$D = k\lambda / (\beta \mathrm{Cos}\theta) \quad (1)$$

where D is the crystallite size, k is a fixed number of 0.9, λ is the X-ray wavelength, θ is the Bragg's angle in degrees, and β is the full-width-at- half maximum (FWHM) of the chosen peak. Compared to the reference data from TiO_2 (JCPD) card, the peaks in the X- Ray diffraction shift into the region of higher 2θ, indicating stress in the grains. Increasing in full-width at half-maximum (FWHM) of (101) peak means decrease crystal size of film with the increase doping concentration in TiO_2 films as shown in Fig. (2). This result agrees well with literature [1]. XRD analysis also did not detect the dopant phase, this is due to the low concentration of dopants, in previous work by other group[1]. Results of TiO_2: Cd at different doping concentration on the films structure is given in Table (1).

The anatase phase is having a tetragonal unit cell and the lattice parameters (a, c) can be calculated from the peak positions (0 0 4) and (2 0 0) using the relations $a = b = 2 \times d_{004}$ and $c = 4 \times d_{200}$ [4, 19]. Increases in doping concentration in TiO_2 films result in the increasing lattice constant (a), this can be attributed to increase in interplanar distance (d) according to above equations. The lattice parameters calculated for the undoped films were a = 3.7914 ˚A and c = 9.5898 ˚A. This is close to the reported bulk values of anatase phase (a = 3.7842 ˚A, c = 9.5146 ˚A). The dependence of the lattice parameters on doping concentration is shown in Fig. 2 B. It can be observed that the lattice constant a decreases with the increasing doping concentration where as the lattice constant c increases with it. In the case of films undoped films the ratio of lattice constants c/a was 2.52 ˚A which is higher than the c/a value (2.5142 ˚A) of the stress free TiO_2. Therefore increases in doping concentration in TiO_2 films lead to increase of the lattice constant ratio c/a these means the lattice under the stress [4]

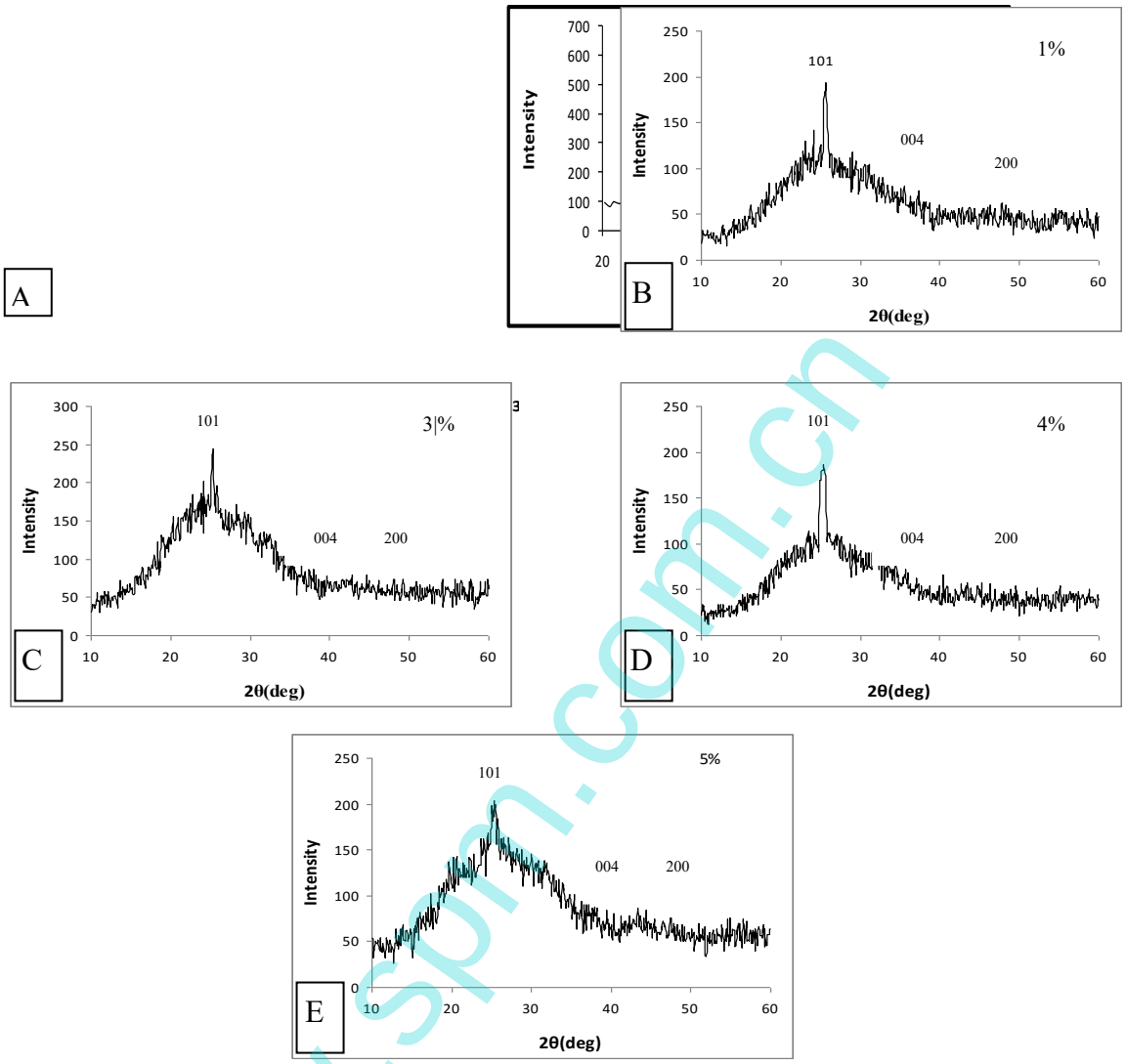

Fig. (1) :XRD patterns of TiO_2 films pure and doping with cadmium at different concentrations(A) TiO_2 pure (B) 1% (C)3% (D)4% (E)5%.

Table(1): Experimental results for TiO_2 at different doping concentrations.

TiO_2 doping with Cd	2(θ) deg	hkl	β (deg)	Crystal size (nm)	a=b (°A)	c (°A)	c/a
Undoped TiO_2	25.27	A(101)	0.272	29.87	3.7914	9.58989	2.5200
1%	25.6116	A(101)	1.11970	7.2822	3.786	9.61188	2.5293
3%	25.1	A(101)	2.400	3.393	3.7803	9.6922	2.5387
4%	25.4268	A(101)	3.54960	2.295	3.7803	9.755	2.5638
5%	24.0258	A(101)	6.75410	1.2030	3.77964	9.804	2.5938

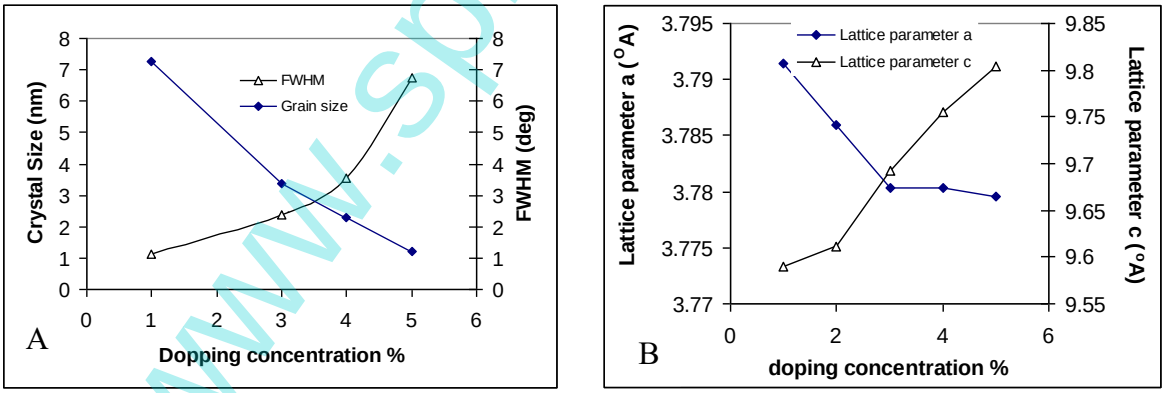

Fig. (2) :(A) The main grain size and Full Width at Half Maximum (FWHM) for TiO_2 films A (101) at different doping concentration of cadmium. (B) The plot of the variation of lattice constants ‘‘a” and ‘‘c” as a function of annealing temperature. The lattice constant ‘‘a” was calculated from the X-ray peak (0 0 4) and lattice constant ‘‘c” was calculated from peak (2 0 0).

3.2. AFM study.

Fig. 3 shows the surface morphology micrographs of undoped and Cd-doped TiO_2 thin films measured by scanning probe microscope with contact mode. It exhibits that all samples have dense grains. The grains are basically round, which grow preferentially along the c-axis orientation perpendicular to the substrates. For the pure TiO_2 thin film as show in Fig. 3(a), the average grain size is about 140 nm and the lateral size distribution is not uniform. The grain size greatly reduces with Cd doping concentration increases. 5% Cd-doped TiO_2 thin film has uniform and dense grains.

AFM results show that by the addition of the Cd to TiO_2 thin films they become smooth where the root mean square (RMS) for undoped and doped with Cd are 0.1658 nm and 0.115 nm respectively. This result agrees well with literature [20].

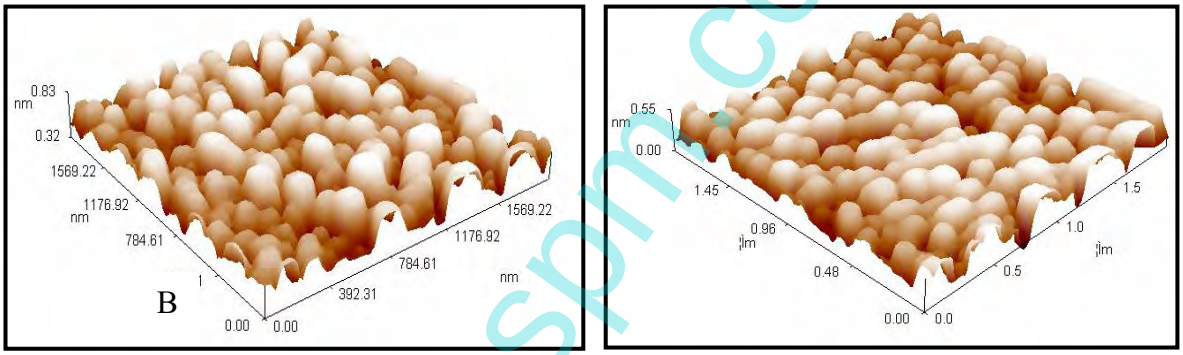

Figure (3) :The AFM images: (A)undopped TiO_2 films (B) TiO_2 doping with cadmium at 5%

3.3. SEM study

Fig. (4) Shows the scanning electron microscopy SEM micrographs of undoped and Cd-doped TiO_2 thin films. The more uniform polyhedral particles of doped TiO_2 could be attributed to slower deposition rate and inhomogeneous nucleation that favor the polyhedral-shaped particles [21]. Films are homogenous and continuous separate coating layers. There seems to be mismatch in average size of crystal determined through Scherer's calculation utilizing XRD data and SEM analysis. SEM image suggest size of crystal to be much larger. It seems appropriate to consider that the particle which appears in SEM images is, in fact, grain agglomerates [22].

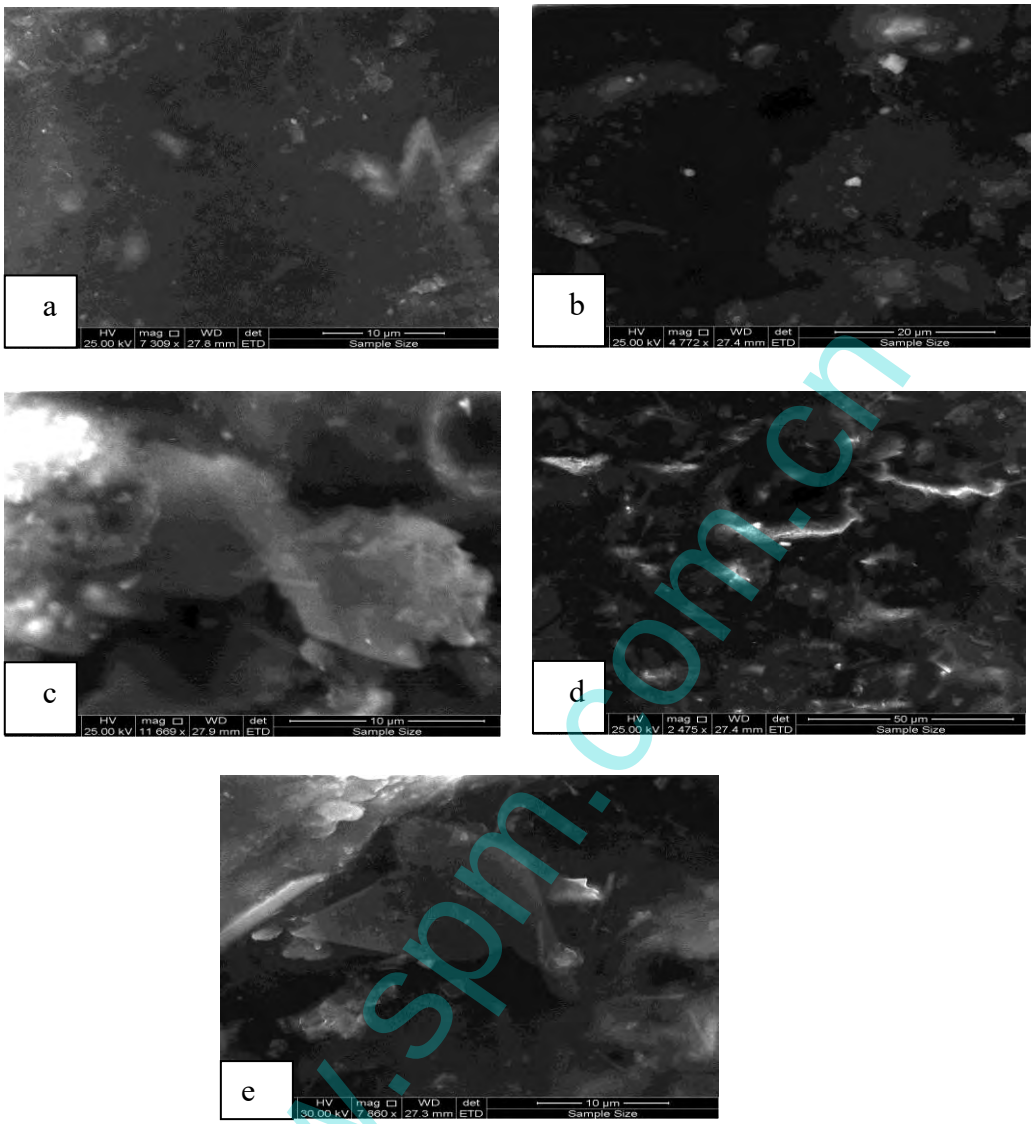

Fig. (4): SEM image of TiO_2 thin film : (a) undoped TiO_2 thin films (b) TiO_2 thin films doping with cadmium at 1% .(c) **TiO_2 thin films doping with cadmium at 3% .** (d) **TiO_2 thin films doping with cadmium at 4% .** (e) **TiO_2 thin films doping with cadmium at 5% .**

3.4. Optical properties

Fig. (5 A) it shows the optical transmittance spectra of TiO2 pure and doping with cadmium at different doping concentration within the wavelength range (300- 1100) nm. The transmittance spectra of the films can be analyzed as follows: For all the films high transmission at long wavelengths. Optical transmissions of all films decreased with decrease in wavelength less than 300 nm doping TiO_2. The transmittance of the TiO_2 thin films increases with the increasing doping

concentration in the films. This effect of doping on the transmission of TiO_2 films can be linked with decreasing in particle size (as shown by x-ray). This is consistent with other reports [23].

The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for TiO2 films, according to the following equation [3].

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \qquad \text{.....(2)}$$

Where d is the thickness of thin film, and T is the transmission. Fig. (5 B) show the absorption coefficient (α) of the TiO_2 thin films (at annealing temperature in 823 K for 120 min for undoped and doped films) with different doping concentration. The absorption coefficient of the films decreased in the visible region because it is inversely proportional to the transmittance, and decreased with increasing doping concentration in the films. This result consists with other research such as [16].

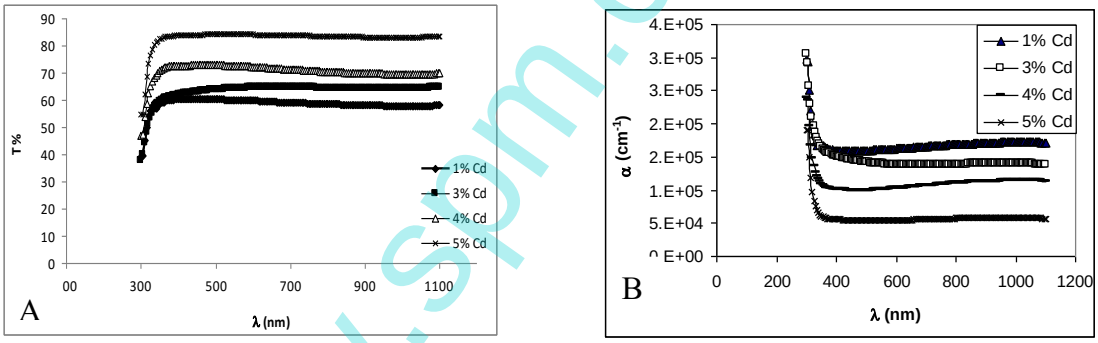

Fig. (5) (|A) Transmittance spectra of TiO_2thin films for different doping concentrations. (B) The optical absorption coefficient as a function of wavelength of TiO_2 thin films for different doping concentrations

Fig. (6A) shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ to determination the optical energy gap for films at different doping concentration (1,2,3,4 and 5 %). The results show increase in energy gap with increase doping concentration of cadmium in TiO_2 films (3.8- 3.86 eV), as shown in Fig. (6 B). We could attribute this to decrease in crystal size (become less crystallinity as is evident from the X – ray diffraction, (effect of quantum confinement) [24]. If this increase in the band gap energy was due to the quantum confinement, an inverse square relation between ΔEg and grain size can be expected [4]

$$\Delta E_g = E_g - E_g\,(bulk) = E_b\left(\frac{\pi a_B}{R}\right)^2 \qquad \text{……..(3)}$$

where E_g is the measured band gap energy in eV, E_g (bulk)is the band gap of bulk material in eV, E_b is the excitation binding energy in eV, a_B is the excitation Bohr radius in (nm) and R is grain radius in nm. ΔE_g was plotted against $1/R^2$ and the graph is presented in Fig. 6(c). Since the plot did not demonstrated a straight-line fit we have ruled out the possibility of quantum confinement [4]. The optical band gap values for different parameters are tabulated in Table (2).

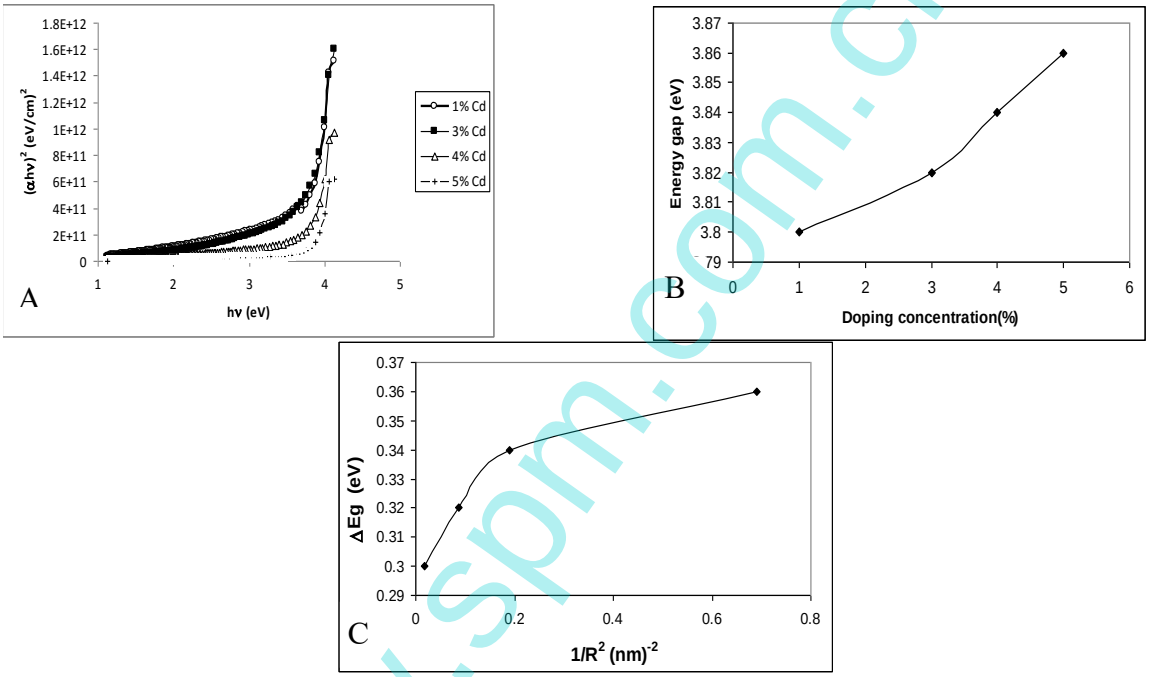

Fig. (6) :(A) $(\alpha h\upsilon)^2$ verses hυ of TiO_2 pure and doping with cadmium. (B) optical energy gap as a function of different doping concentrations.(C) Plot of ΔE_g against inverse square of the grain radius ($1/R^2$) of the TiO_2 films of different doping concentrations.

Table (2): Experimental results of TiO_2 thin films doping with cadmium.

doping concentrations	E_g(ev)
undoped	3.5
1%	3.8
3%	3.82
4%	3.84
5%	3.86

3.5. Electrical properties

In order to investigate the effect of cadmium doping on some electrical properties of TiO_2 films, electrical resistivity as a function of doping concentrations Cd as shown in Fig. (7). The resistivity was measured using relation $\rho = \pi/\ln 2(V/I)t$ [16] where V is the applied voltage, I the current, and *t* the film thickness of the film. From figure shows that the electrical resistivity is decreased with increasing Cd doping concentration (Cd) in TiO_2 thin films. This could be attributed to the increasing in charge concentration.

Fig. (8) Indicates the variation in the electrical resistivity of TiO_2 films with temperature for different doping concentration. The resistivity decreases as the temperature is increased. This is due to the increase in the excitation of the charge carrier which will increase the probability of transition from valence band to conduction band. From the relationship between $\ln \rho$ and 1000/T for TiO_2 films, which calculate the activation energy (E_a). The activation energy E_{a1} is found to be in the range (0.197-0.0844 eV). From this it can be inferred that the TiO_2 Fermi level is far to the band gap center (Eg/2), because that the TiO_2 is extransic state this is consistent with the above

results for the electrical resistivity, also these values of activation energy are in agreement with the previous works [2] . Table (3) shows the activation energy E_{a1} and E_{a2} of the TiO_2 thin films doped with cadmium.

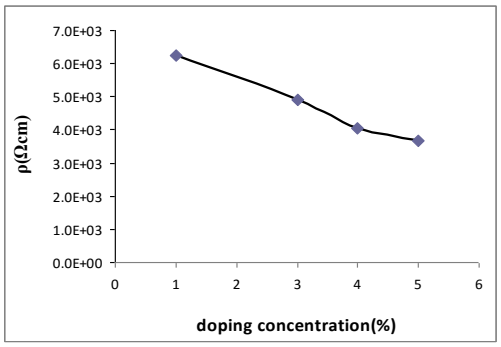

Fig. (7): The electrical resistivity as a function of different Cd doping concentration for TiO_2 films.

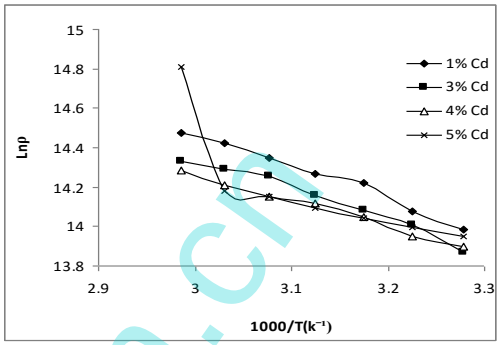

Fig. (8): Ln ρ as a function of 1000/T(K)$^{-1}$ for TiO_2 films at different Cd doping concentrations for TiO_2 films.

Table (3) : Activation energies Ea_1 and Ea_2 for TiO_2 at different doping concentrations.

Doping with cadmium	E_{a1}(eV)	E_{a2}(eV)
undoped	0.0502	0.0526
1%	0.1972	0.1301
3% $_2$	0.1597	0.0726
4%	0.1263	0.1290
5%	0.0844	1.2034

3.6. Photocatalytic activity

The photocatalytic reaction is very sensitive to the catalyst surface. The reaction is initiated by the production of electron hole pair on TiO_2 surface which results from the absorption of photon with

energy equal or greater than the band gap. The MB reacts with electrons generated on the TiO_2 particles under UV irradiation. Fig. 9 shows the absorbance of MB at 605 nm as a function of UV light irradiation time on the TiO_2 films immersed in the solution. The absorbance spectra of the MB (100 mg/l) solution degraded with the TiO_2 film which is shown in the inset of Fig. 9. In order to demonstrate the degradation process, the spectra was recorded at different time intervals. The experiment was repeated with two sets of films at identical conditions and the results were reproducible. From Fig. 9 it can be observed that the absorbance decreases with light irradiation time, which indicates the photodegradation of MB. Further it can be observed that the rate of decrease in absorbance is significant in the case of films at high doping concentration. The diminishing of the absorbance band at 605 nm is very noticeable indicating good photocatalytic activity. The photocatalytic experiments show that the photocatalytic activity of Cd-doped TiO_2 thin films has been enhanced compared with that of undoped TiO_2 thin films. This enhancement should be attributed to the increase of specific surface area [25].

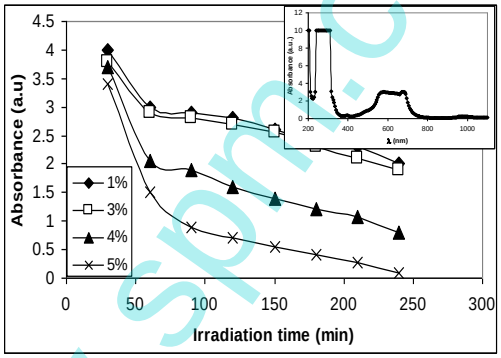

Fig. 9. Absorbance at 605 nm of an aqueous methylene blue solution (MB) as a function of UV light irradiation time of the TiO_2 films immersed in it. Inset: absorption spectra of aqueous MB solution (100 mg/l) degraded by a TiO_2 film at doping concentration 5%.

4. Conclusions

Titanium oxide thin films were prepared by spray pyrolysis technique on quartz substrate at 623 K. the effect of Cd doping on structure, electrical, optical, and photpcatalytic properties of TiO2 thin films were studied by XRD, AFM, SEM, four probe and UV- Visible measurements. The major observations of this study can be summarized as follows. The grain size showed dependence on

doping concentration, the XRD results reveal that the deposited thin film of TiO_2 has anatase structure. Band gap of the film increased from 3.5 to 3.86 eV after doping, which is higher than the values, reported in the literature. Atomic force microscope (AFM) results show that the addition of the Cd to TiO_2 thin films become smooth. The high band gap observed in this study can be correlated with the nanocrystalline nature of the films (effect of quantum confinement).The effect of doping the TiO_2 film may enhance the photoresponse and can have positive results on the photocatalytic activity.

5. References

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