J Nanostruct 14(1): 168-175, Winter 2024

RESEARCH PAPER

Investigation of the Characteristics of the Prepared TiO_2/ Graphene Films by Spin Coating Method

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ARTICLE INFO

Article History:
Received 04 October 2023
Accepted 23 December 2023
Published 01 January 2024

Keywords:
Hydrothermal method
Optical properties
Spin coating
Structural properties
TiO_2/graphene films

ABSTRACT

Titanium dioxide/Graphene composite films were prepared utilizing two steps (Hydrothermal and spin coating) methods FTO glass substrates for (1, 2, 3, and 4) layers, with sequential thermal treatment. The produced films were characterized using X-ray diffraction, where the dominant phase was (011) with a crystalline size of 38.6 nm for (1, 2, and 3) layers. While for 4 layers was (004) with 36.92 nm. In general, the increasing of layers and the heating treatments affected the crystalline size of that deposited on FTO glass, where swing between the two values (27 and 36) nm, without the appearance of any peaks of graphene. In addition, the morphological properties were determined by transmission electron microscopy. The scanning electron microscopy images of the prepared films showed the dependence of both partial size and porosity on the number of layers. Despite reducing the gap energy of the 1layer film compared to TiO_2 gap energy. However, the energy gap of the (2, 3, and 4) layer films increased to about 3 eV, where the increase in layers number over one layer and the thermal treatment did not affect a noticeable change in the gap energy.

How to cite this article
Hussian S., Al-bahrani M. Investigation of the Characteristics of the Prepared TiO_2/Graphene Films by Spin Coating Method. J Nanostruct, 2024; 14(1):168-175. DOI: 10.22052/JNS.2024.01.017

INTRODUCTION

Titanium dioxide (TiO_2) is one of the transition metal oxides, which has perfect optical properties in the ultraviolet (about 3.7 eV) [1], however, the key challenge that most significant challenge that creates limitations in optical applications is the fast recombination of the photogenerated e-h. Thus, the researchers proposed several mechanisms; (i) the transition metal doping such as Ni, Co, Fe, Mo, Nb, and Ru [2]. Ions of these metals may create active traps leading to increasing the recombination that will be affecting the photocatalytic efficiency. (ii) Noble metallic nanoparticles such as gold, copper, and silver [3], in this case, the photogenerated electrons are likely to be attracted to particle surfaces which makes recombination so fast. (iii) The mechanism with the best results was to provide a transition surface for the excited electrons. Graphene was the most potential candidate [4].

Graphene has unique physical properties; high thermal conductivity [5] ، high charge carrier mobility [6,7] and optical transmittance of almost 97% [5] with about 0.1% of reflectivity [6][8]. In general, for TiO_2/ Graphene (TiO_2/ G) composite, the transition of excited electrons depends on the presence of UV or visible light and oxygen findings that are reduced by graphene as explained in Fig.

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1 [9] [10][11].

In the recent decade, TiO_2/ G composite was prepared via several methods for photocatalytic degradation, photocatalytic, gas sensing, and self-cleaning applications, as explained in Table 1.

In this work, we present a discussion of the characteristics of TiO_2/ G composite films that were Prepared via the spin coating method.

MATERIAL AND METHODS

Materials

The spherical TiO_2 nanoparticles (Anatase) (TiO_2, 99.5%, 10-30 nm) and ethanol (99.9%) were supplied by Sigma Aldrich. Whereas, the nanosheets graphene (G, 15 micros) with a platelet morphology were obtained from (sky spring Nanomaterials).

Synthesis of TGr composite films

Synthesis of TiO_2/ G composite, a mixture of 0.02g of graphene, 1g of TiO_2, and 4 ml of ethanol (99.9%) was sonicated for 20 min at room temperature. Then, the produced solution was pleased into an autoclave with adding of 50 mL of distilled water (DW). So, the reaction has been achieved under 160 °C for 72 h, then gradually cool

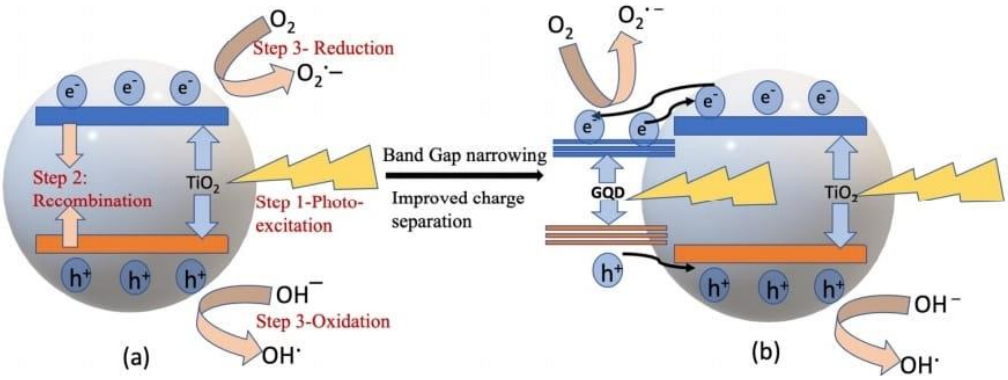

Fig. 1. Scheme to illustrate the mechanism of electron transfer in TiO_2/ G composite [9]

Table 1. TiO_2/ G composite preparation and applications

Year	Authors	Method	Application	Ref.
2016	Oliveira et al.	electrochemical	photocatalytic	[10]
2016	Shanmugam et al.	in-situ microwave	photocatalytic degradation	[11]
2017	Amiri and Ashkarran	Sol-Gel/spin coating	gas sensing	[12]
2017	Hu et al.	hydrothermal	photocatalytic degradation	[13]
2019	Ghayoor et al.	modified Hummers	solar cell	[14]
2019	Giampiccolo et al.	Sol–Gel	the photocatalytic-assisted sensing	[15]
2020	Molina et al.	liquid phase deposition	Photodegradation	[16]
2020	Liu et al.	hydrothermal	photocatalytic degradation	[17]
2020	Xiongfeng et al.	sol	photocatalytic degradation	[18]
2020	Mandujano and Rodriguez	assisted by ultrasound	photocatalysis	[19]
2021	Dai et al.	non-solvent induced phase-separation	photocatalytic degradation	[20]
2021	Zhao et al.	Sol-Gel under ultrasonic radiation	photocathodic protection, and superhydrophobicity	[21]
2022	Li et al.	Sol-Gel		[22]

Table 2. the thermal steps protocol.

Thermal increasing (°C)	Thermal zone (°C)	Time life in the thermal zone (min)
40-80	80	10
80-120	120	10
120-250	250	15
250-375	250	30
375-450	450	30

down to room temperature, filtered, and washed with DW and ethanol several times directly. Then, dried overnight at 40 °C. TiO_2/ G composite powder (0.5g) was added to 30ml ethanol on a magnetic stirrer until complete dissolution. TiO_2/ G composite films were synthesized by spin coating with 2650 rpm of speed for 10 minutes, 1000 rpm/min of acceleration, and adding 500 µL of TiO_2/ G composite solution (drop by drop). Then the synthesized films were treated thermally employing the thermal steps protocol for every four layers. Then, were leavened to cool gradually to room temperature throughout the night-down. Table 2 represents the thermal steps protocol.

Characterizations

TiO_2/ G composite films have been characterized structurally by utilizing an X-ray diffractometer (XRD) with 4 degrees per minute of scan speed, Cu Kα1 radiation (λ=1.54060 Å), 30 kV, and 10 mA), and morphologically via studying transmission electron microscopy (TEM) and scanning electron microscopy SEM images. In addition, utilizing UV–Vis spectroscopy to determine the optical properties.

RESULTS AND DISCUSSION

X-ray Diffraction

Fig. 2 illustrates the XRD patterns of the prepared films on substrates of glass (one layer) and FTO glass (1, 2, 3, and 4) layers. However, the deposited films on the glass substrate showed a polycrystalline structure of nanocrystalline, anatase (TiO_2) with a dominant phase at 2θ=25.23(011) according to ICDS 98-009-2363 cared [23] and crystalline size of 38.6 nm. In the same position, the dominant peaks emerged with a blue shift with (Δ2θ ≈1.3°) of average in all (1, 2, and 3) layers and appearing of SnO_2 at 2θ ≈33.893° and 61.872° with (310) (101) respectively according to ICDD 00-041-1445 card that points out to FTO. While for four layers on FTO glass, the dominant phase emerged at 2θ = 37.89° (004) with 36.92 nm of crystalline size. In general, the increasing of layers and the heating treatment affected the crystalline size of that deposited on FTO glass, where swing between the two values (27 and 36) nm. We believe that the annealing is responsible for the displacement of the TiO_2 peaks as a result of the acquisition of high kinetic energy by both graphene and titanium oxide particles, which primarily led to the oxidation of graphene.

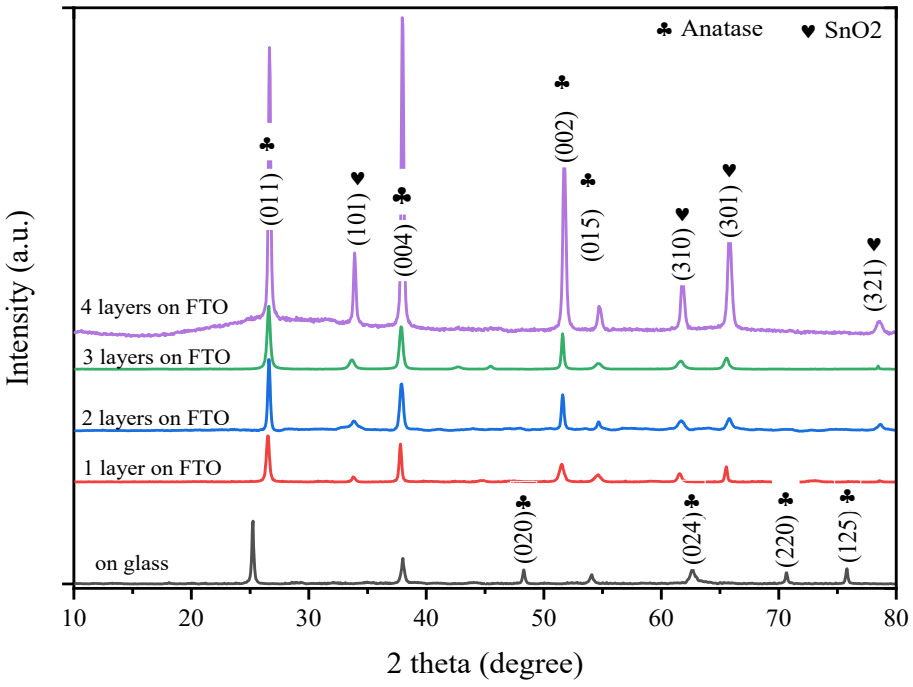

Fig. 2. The XRD patterns of the prepared films on substrates of glass (one layer) and FTO glass (1, 2, 3, and 4) layers

TEM and SEM images

TEM image of the stripped-off particles of the deposited film on the glass substrate shows the spherical clusters with 89.15±37 nm of the average size of clusters that consist of spherical particles with 20.8±6.5 nm of the average size of particles (Fig. 3a and b). The selected area electron diffraction (SAED) confirmed the crystallization indicated by XRD analysis in Fig. 2 as shown in Fig. 3c. For the deposited film on the glass substrate, the SEM image (Fig. 4) showed both shapes and types of particles formed, which it is composed of polygonal particles with (78.00±60.62) nm in a dark appearance. Conversely, the bright particles consist of needle shapes and big particles that are believed to be graphene particles.

Fig. 5 illustrates the surfaces of the deposited films of (1, 2, 3, and 4) layers on FTO glass substrates.

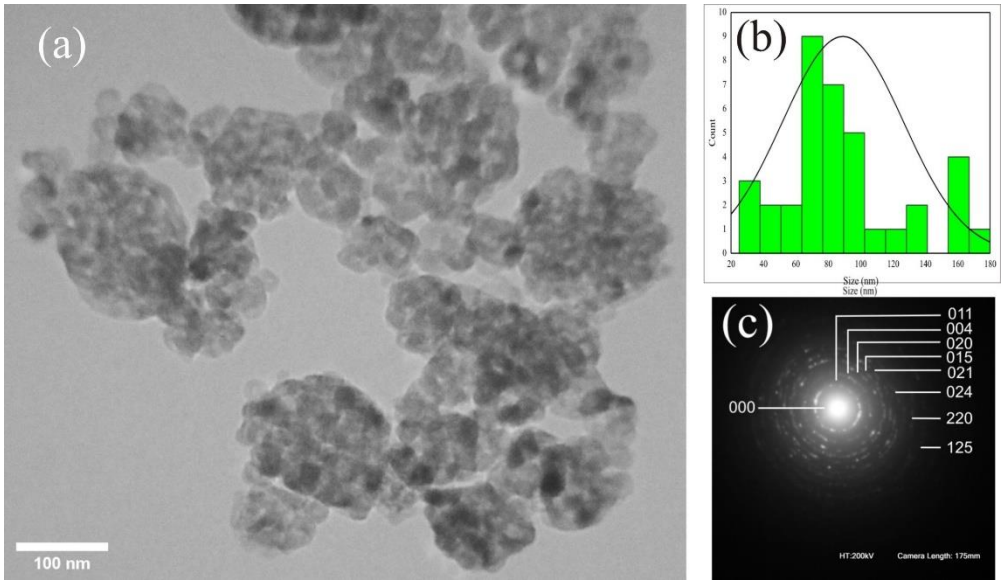

Fig. 3. (a) TEM image of the stripped-off particles of the deposited film on the glass substrate, (b) the size distribution diagram, and (c) SAED.

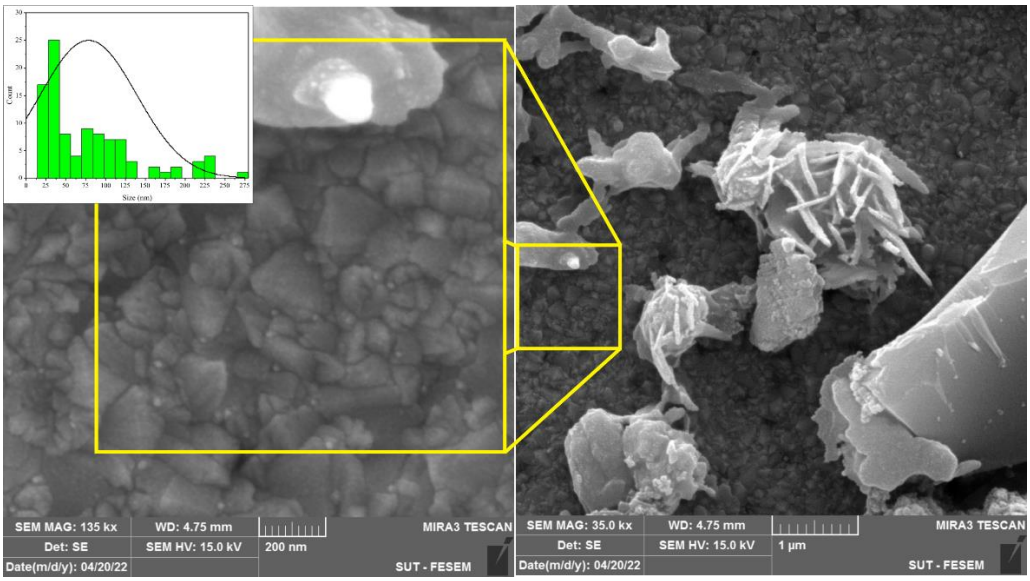

Fig. 4. SEM image of the deposited film on the glass substrate

It is clear that there is a difference between the surfaces of the films according to the number of layers that attributes to two causes; change in the roughness of the surface with the accumulation of layers, adding to the heat treatment sequence. In addition, it is noticeable that the number of layers affects the values of all the average particle size, shape, and porosity, where the average particle size increases depending on the number of layers (19±17.9, 20.55±20.8, 50.3±23.6, 63.21±28.1) nm. Nevertheless, the surface porosity fluctuated (62.78, 73.43, 48.44, 66.75) % respectively. It is worth noting also, it was observed in Fig. 5 (a and b), that there are cracks believed to be due to the difference in the tension coefficients between the coated TiO_2/ G composite layer and the substrate.

The thickness was determined using the cross-section images of the deposited films. Where increase with the increasing number of layers (7.53±1.86, 14.38±1.89, 314.62±31.53, 702.78±43.48) nm for (1, 2, 3, and 4) layers, as shown in Fig. 6.

Optical properties

Fig. 7 shows the transmittance of the prepared films one layer (1L), two layers (2L), three layers (3L), and four layers (4L) respectively for (300 to 1000) nm. It is evident that the absorption coefficient (α) is greater than 10^4 cm^{-1} (as shown in the mini figure in Fig. 7), according to equation

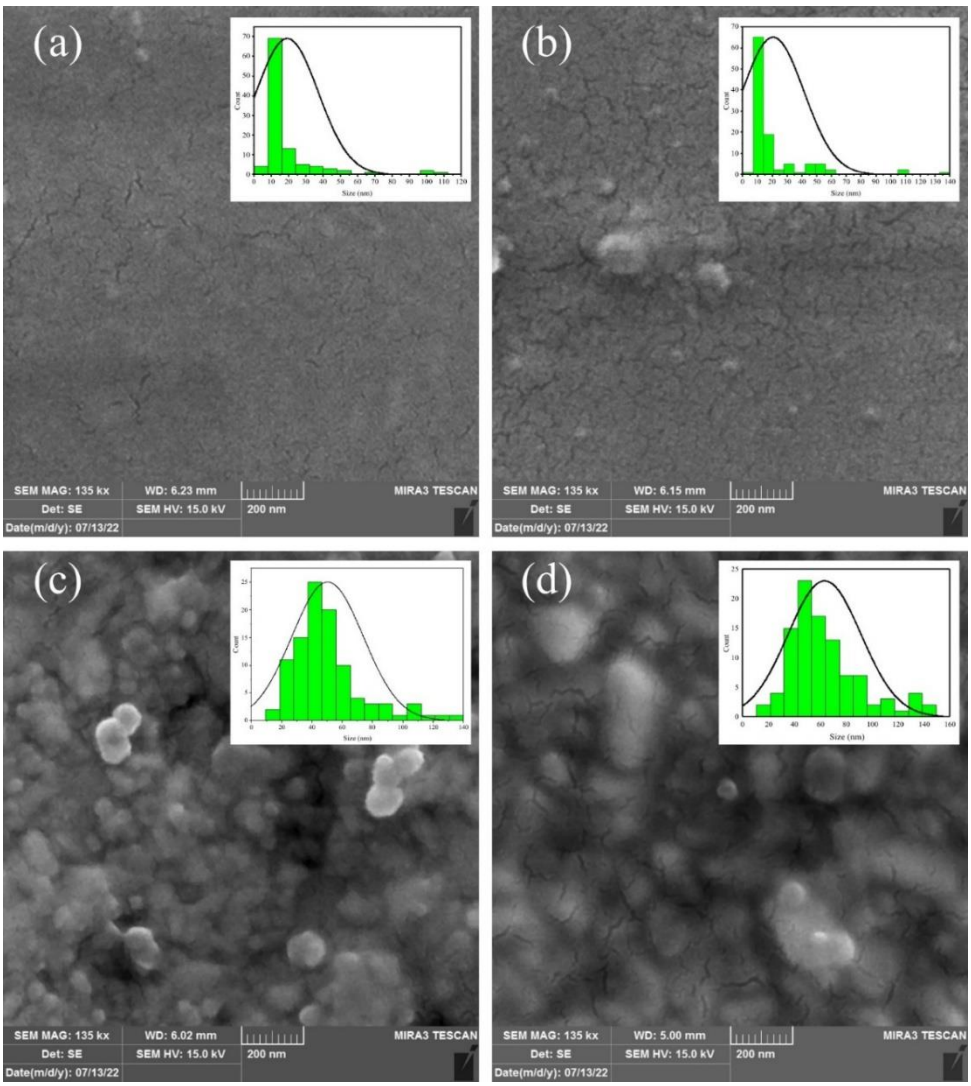

Fig. 5. the surfaces of the deposited films of (1, 2, 3, and 4) layers on FTO glass substrates.

(1), which refers to having a direct optical gap [24].

$$\alpha = 2 \cdot 303 \frac{A}{d} \quad (1)$$

where (A) is the absorbance and (d) is the thickness of the film. Due to the relative height optical bandgap (E_g), was calculated according to equation (2)[25].

$$(\alpha hv)^2 = B(hv - E_g) \quad (2)$$

Accordingly, that resulted to have a height transmittance. In general, the transmittance

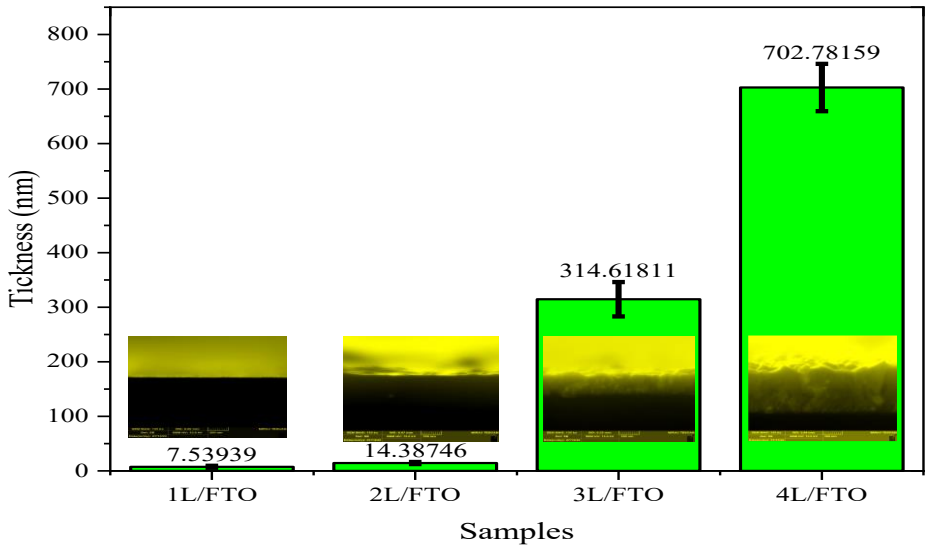

Fig. 6. The thickness of the prepared TiO_2/ G composite films, the minimized images represent the cross-section of the prepared films

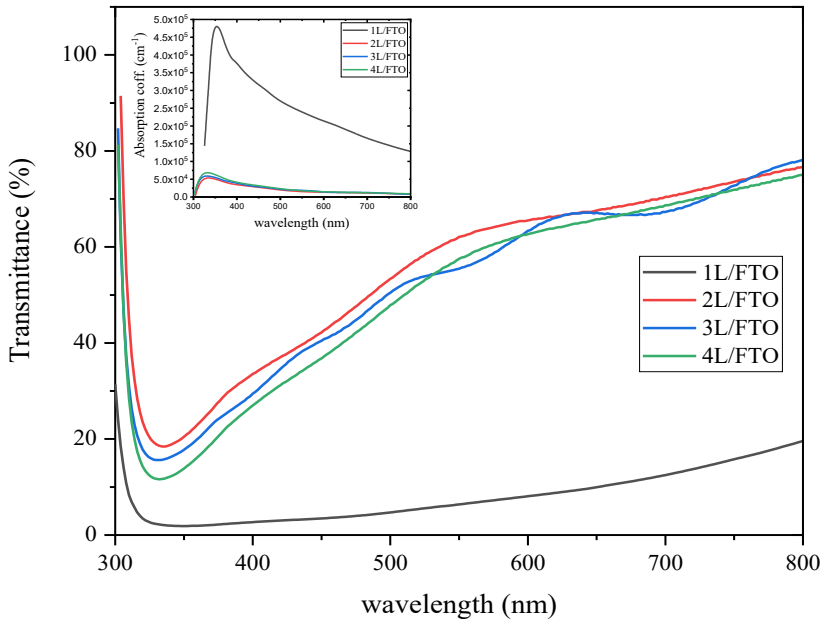

Fig. 7. The transmittance of the prepared films (1L, 2L, 3L, and 4L).

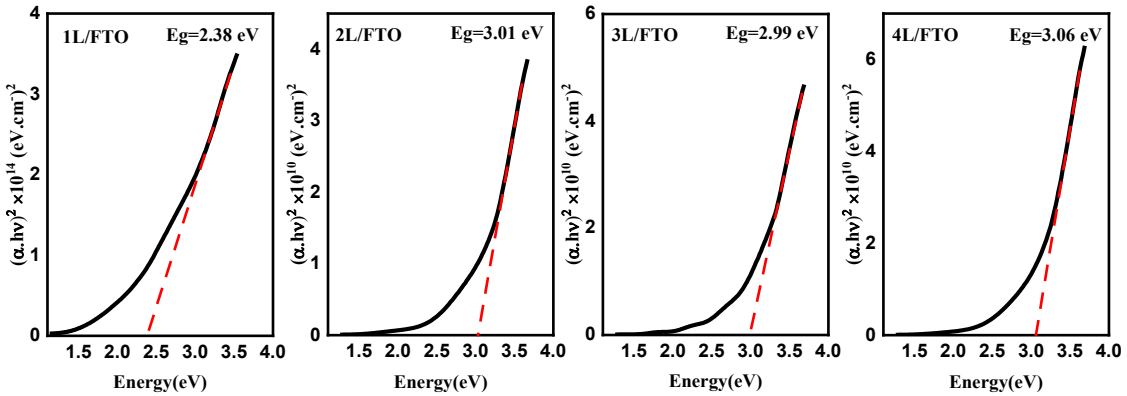

Fig. 8. the energy gap of the prepared films (1L, 2L, 3L, and 4L).

behavior was enhanced with the increase of the layers number increasing, which increased from 2.21% at 375 nm of wavelength for 1L to (27.9, 24.15, and 20.75) % for 2L, 3L, and 4L respectively. While it increased from 6.57% for 1L at 550 nm of wavelength to (55 – 62.5) % as for 3L and 2L respectively.

There is a noticeable change in the energy gap value between it in 1L and other layers. As well, increasing in the layers and the thermal treatment did not noticeable effect on the energy gap despite the obvious fluctuation in porosity values, where, they were (2.38, 3.01, 2.99, and 3.06) eV for 1L, 2L, 3L, and 4L respectively as shown in Fig. 8.

CONCLUSION

TiO_2/graphene films were successfully prepared by utilizing a combination of both hydrothermal and spin coating methods, with thermal treatment for several layers. Both increases in layer number and the thermal treatment enhanced the prepared films' optical properties, which could qualify these films as effective layers in solar cells and photovoltaic applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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