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Optical Investigation of TiO_2/Graphene Oxide Thinfilm Prepared by Spin Coating Technique

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Optical Investigation of TiO_2/Graphene Oxide Thinfilm Prepared by Spin Coating Technique

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Abstract

Titanium dioxide/graphene oxide thin films with different concentrations of (0.0, 0.015, 0.030, 0.045 and 4.5 g/ml) graphene oxide were deposited on glass substrates at room temperature using spin coating method. Thin films were characterized by UV-Vis, FTIR and Raman spectroscopy. Presence of graphene oxide was confirmed with FTIR and Raman spectroscopy, too. The optical band gap of TiO_2 with the addition of graphene oxide layer initially decreases, but by increasing the concentration of graphene oxide, the optical band gap increases to 2.9eV.

Keywords: TiO_2/GO, spin coating method, optical properties.

1. Introduction

Titanium dioxide is one of the transition metal oxides, that because of specific electronic and optical properties, was considered by the researchers [1-4]. TiO_2 thin layer has the high transparency (70%-100%) in the visible wavelength region (600nm-800nm). The optical band gaps of anatase, rutile and brookite phases are 3.2eV, 3eV and 3.3eV, respectively. Titania due to its high refractive index (2.49 and 2.9 for the anatase and rutile phases, respectively), was considered in optical applications [5-7]. The high refractive index of TiO_2, along with absorption of light in the visible range, is one of factors that make it a white pigment. [2, 8 and 9].

Guang et al. synthesized TiO_2 thin films by electron beam evaporation method. Their results were indicated that with the increase in the TiO_2 grain size, its band gap shifts from 3.4 to 3.21eV [2]. Titanium dioxide is a suitable candidate for using in solar cells and photo-voltaic devices because it has a relatively high efficiency and good stability [10-12]. The band gap of titania is about 3.2eV. By reducing the band gap value, it can absorb the sunlight more and increase its efficiency [8]. To reduce the band gap and improve titania properties, it is combined with different materials. Among the various materials that can be selected, carbon structures have advantages such as chemical stability in different ambiences. One of the carbon nanostructures is graphene that was discovered in 2004, which has special properties such as high electrical conductivity, high thermal conductivity, high mechanical strength and high surface area [13-14]. The effect of adding graphene and graphene oxide on the optical band gap of titanium dioxide is very little investigated by the researchers. Combination of TiO_2 and GO (Graphene Oxide) can have many applications, especially in the solar cell area [12]. For example, Timoumi et al. prepared TiO_2-GO nanocomposite thin films by spin coating method. Their results indicated that by increasing the amount of graphene oxide, the band gap energy is reduced from 3.62eV to 1.40eV. TiO_2-GO has significant optical properties because of the life span of the electron-hole pair is greater than that of pure TiO_2 [15].

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2. Experimental details

2.1 Preparation of TiO_2 Solution: Titanium dioxide solution was prepared by following the previously reported procedure [1].

2.2 TiO_2 deposition conditions: The glass substrate was washed using ultrasonic bath for 30min at 60°C and then washed in acetone for 5min. TiO_2 was deposited by spin coating method with speed of 5000 rpm on the substrate. Deposition was performed for 1min and 30 repetitions. These layers were calcined at 550°C for 1 hour.

2.3 Preparation of graphene oxide: Graphene oxide colloid was synthesized with the concentration of 1g/ml by modified Hummer method using graphite and potassium permanganate as precursors. For preparing graphene oxide sol with various concentrations of 0.015, 0.030, 0.045 and 4.5 g/ml, different amounts 0.15, 0.3, 0.45 and 45 gram of graphene oxide colloid was mixed with 10 ml ethanol and dispersed for 10 min in ultrasonic dispersion.

2.4 Graphene oxide deposition conditions: Graphene oxide solution with different concentrations on the TiO_2 thin films was deposited by spin coating method. The deposition was deformed at a speed of 5000 rpm and for 1min. The final layers were placed at 40-50°C for 30 min.

2.5 Characterization: The infrared spectra was recorded by using Fourier-transformed infrared spectrophotometer (AVATAR 370, Thermo Nicolet) in transmission mode in the wave number range 4000-500 cm^{-1}. Optical properties such as absorption and transmission spectra of the samples were studied using UV-Vis device U3500 model. Room temperature Raman spectra were measured by using a micro-laser Raman spectrometer (Takram P50C0R10) in a back scattering configuration employing the 532 nm line of Nd:YAG laser as excitation source.

3. Rsults and Disscussion

3.1 Raman Spectroscopy:

As shown in Fig. 1 Raman spectra of TiO_2/GO thin films with concentrations of 0.045 and 4.5g/ml prepared by spin coating method on a glass substrate. The obtained results shows that Raman peaks at wave numbers of 135cm^{-1}, 392cm^{-1}, 514cm^{-1} and 634cm^{-1} have good agreement with the standard values of TiO_2 in anatase Phase, which are referred to E_g, B_{1g}, B_{1g}+A_{1g} and E_g modes, respectively. These peaks are sharp and have good intensity indicating that the TiO_2 microstructure in the deposition process is well crystallized. The presence of G and D peaks at wave number of 1592 cm^{-1} and 1350 cm^{-1} indicate the formation of graphene oxide platelets. The G-band is a characteristic of graphite sheets that confirm the presence of the **sp^2** carbon structure. The D-band is related to the existence of defects in the hexagonal structure of graphite. As shown in Fig. 1, the intensity of the D-band is comparable to the intensity of G-band. Therefore, the graphene oxide layers have significant defects. The disorder degree of carbon structure was specified by calculating the intensity ratio of D/G. In this structure, the ratio of D/G is high, that indicating the high degree of irregularity in the structure [1, 16-18].

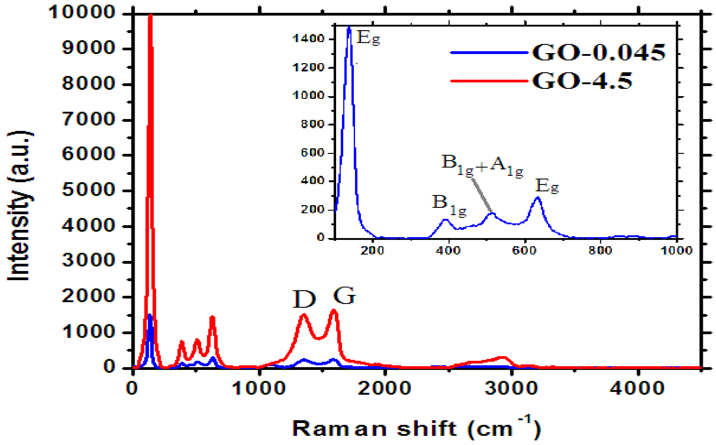

Figure 1: Raman spectra of (a) TiO_2/GO-0.045 and (b) TiO_2/GO-4.5 thin films

3.2 Chemical properties:

FTIR spectra of TiO_2/GO thin films with different concentrations are shown in FIG.2. The FTIR spectrum of TiO_2 thin films in Figure 2(a) shows that there is only one peak in 482Cm^{-1} that is related to tensile vibration of Ti-O-Ti. The FTIR spectrum of TiO_2 /GO thin films with concentration of 0.015, 0.030 and 0.045 g/ml is shown in Fig. 2(b). By adding 0.015g/ml of graphene oxide, O-H (hydroxyl groups) at the wave number of 3443Cm^{-1} can be seen. By adding the concentration of graphene oxide up to 0.045 g/ml, C=N=O peak in the wave number of about 2335Cm^{-1} is also observed. With increasing the GO concentration up to 4.5g/ml (Fig. 2c), it is observed that Ti-O, C-O, C-H, C=C, C-H, O-H peaks are observed at the wave numbers of 656Cm^{-1}, 1059Cm^{-1}, 1428Cm^{-1}, 1629Cm^{-1}, 2905Cm^{-1} and 3434 Cm^{-1}, respectively. The Peak that can be seen at around the wave number of 500Cm^{-1} for all the samples is the characteristic of TiO_2 structure. The presence of the hydroxyl and carbonyl groups in Fig. 2(b) and 2(c) represent the presence of graphene oxide on the surface of TiO_2 [19-22]. Fourier transformers are one of the most widely used infrared devices that can analyze the entire spectral range with using the interferometer system.

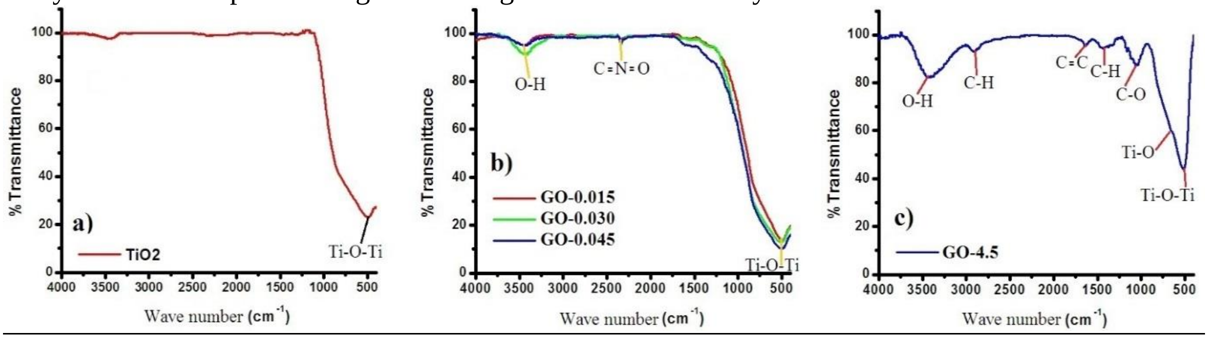

Figure 2: FTIR spectra of (a) TiO_2 (b) TiO_2/GO-0.015, TiO_2/GO-0.030, TiO_2/GO-0.045 and (c) TiO_2/GO-4.5 thin films

Infrared spectroscopy is used to identify molecular species, especially organic species, using the functional groups. In other words, this kind of spectroscopy can identify the various functional groups in the molecular compositions and, as a result, determine the possible structure of the compounds. The peaks in the range of 400 to 1200Cm^{-1} are undoubtedly related to specific functional groups. Peaks in this area are located in a small range, so it is easy to identify the presence of this functional group in the sample. A region that the range of wave numbers is less than 1200 Cm^{-1}, usually involves large and complex peaks that are difficult to interpret. For each particular composition, there is a unique pattern of peaks. This area called the fingerprint area that is used to validate the proposed structure.

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3.3 Optical Properties:

In the Fig. 3, absorption spectra of titanium dioxide / graphene oxide thin films have shown with the various concentrations. The optical absorption edge of the thin films is in the range of 340 nm. According to figure 5, by adding graphene oxide thin film, the absorption of the layers increases and the TiO_2/GO-4.5 thin film has the highest absorption. The absorption peak of this sample is in 233nm, which confirms the presence of graphene oxide and refers to the л to л* transition from the C=C connection that is reported by others [23]. Fig. 4 shows the transmission spectra of titanium dioxide/graphene oxide thin films with different concentrations. In the presence of graphene oxide, the transmittance ratio of the sample increases, but by increasing the concentration of graphene oxide, the transmittance ratio reduces. TiO_2/GO-0.015 thin film has the highest transmission and TiO_2/GO-4.5 thin film has the lowest transmission due to the growth of graphene oxide particles [24]. The transmittance of all the prepared samples is about 20-25% in the visible area.

In order to calculate the optical band gap and determine its type, the optical absorption coefficient of the layers, α (λ), was calculated using the following equation:

$$\alpha(\lambda)= 2.303\, A/\boldsymbol{t}$$

In this formula, A is the absorption and ***t*** is the thickness of the film. Also, E_g can obtained from Tauc formula:

$$\alpha h\upsilon=\beta(Eg-h\upsilon)^n$$

In this relation, β is a constant which is independent of optical band gap energy and n is a constant that determines the type of optical transition and its value is equal to 2 and ½ for the direct and indirect transition, respectively. According to Tauc formula, $(\alpha h\upsilon)^2$ diagram should be drawn up according to (hν) [6, 25]. The optical band gap of titanium dioxide/graphene oxide thin films with different concentrations is shown in Fig 5. According to this figure, TiO_2 has a band gap of 2.62eV. By adding graphene oxide, the optical band gap value decreases to 2.42eV. By changing the concentration of graphene oxide from 0.015 to 0.045 g/ml, the band gaps do not change, but with increasing the concentration to 4.5 g/ml, the band gap increases and reaches to 2.9eV. The addition of graphene oxide increases the capacity of visible light absorption in the TiO_2 thin films, that due to the presence of functional groups on the surface of the grraphene oxide sheets. Some of the л electrons without pairing were connected with the free electrons of the TiO_2 surface, so, the edge of the valence band shift upward and the band gap value decreases. Graphene has a band gap of zero, but graphene oxide has a controllable band gap due to presence of functional groups, that is a great advantage, and this advantage causing use of it for many applications in various fields such as nano-electronics and sensors. Abaidi et al. reported that the band gap of graphene oxide solution and thin film are equal to 3.5eV and 2.2eV, respectively [26]. Timoumi calculated the band gap of TiO_2/GO nanocomposite and obtained it equal to 2eV, while the band gap of TiO_2 is 3.67eV [30]. In the other report from Timoumi and his colleagues, the TiO_2/GO nanocomposite was deposited by spin coating method, and the band gap was obtained using Tauc formula. Their results indicate that the band gap of TiO_2 in the presence of GO decreases, so that by adding 20% GO, its band gap reached to 1.4eV [12]. Similar works were not found for comparing the optical properties of TiO_2/GO heterostructure with this work.

IOP Conf. Series: Materials Science and Engineering **871** (2020) 012087 doi:10.1088/1757-899X/871/1/012087

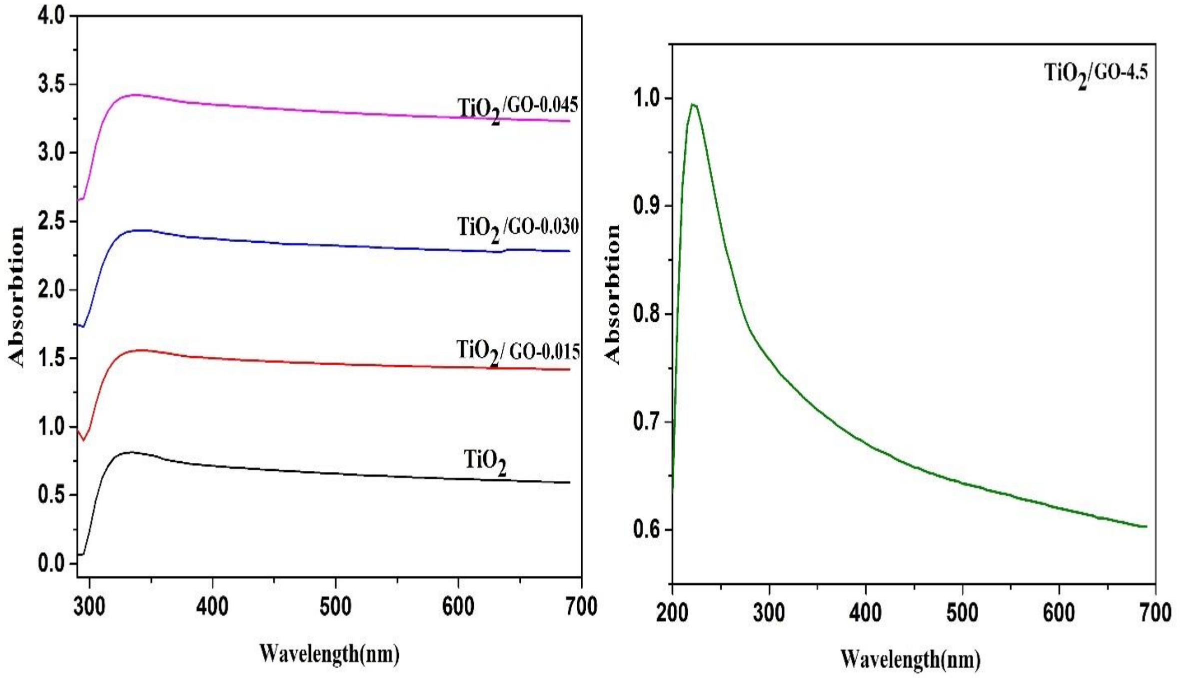

Figure 3: Absorption spectra versus wavelength for different the amount of TiO_2/GO thin films

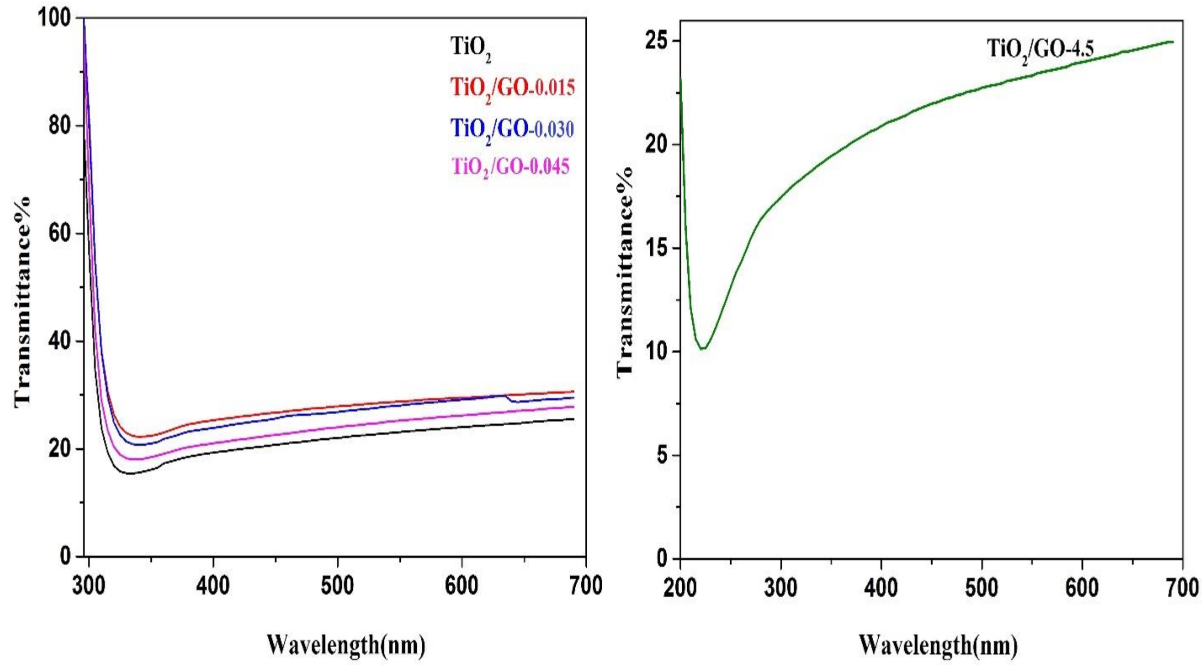

Figure 4: Transmittance spectra versus wavelength for different the amounts of TiO_2/GO thin films

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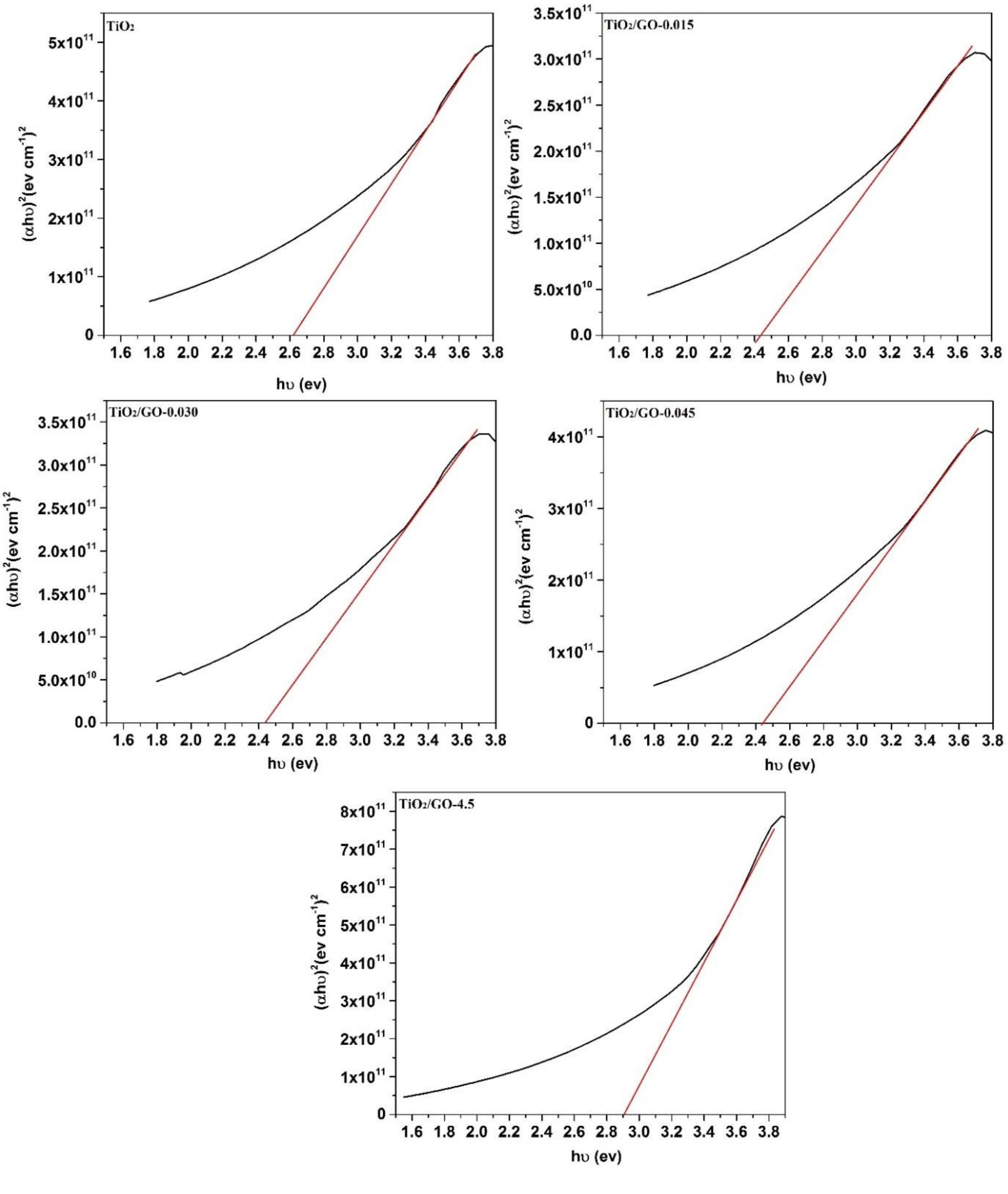

Figure 5: Optical band gap for different the amounts of TiO_2/GO thin films

Fig. 6 shows the amount of thickness ***t*** with respect to the cross-section images for TiO_2 and TiO_2/GO, the values of these layers between 100 to140 nm is considered and is incorporated in the absorption coefficient formula.

IOP Conf. Series: Materials Science and Engineering **871** (2020) 012087 doi:10.1088/1757-899X/871/1/012087

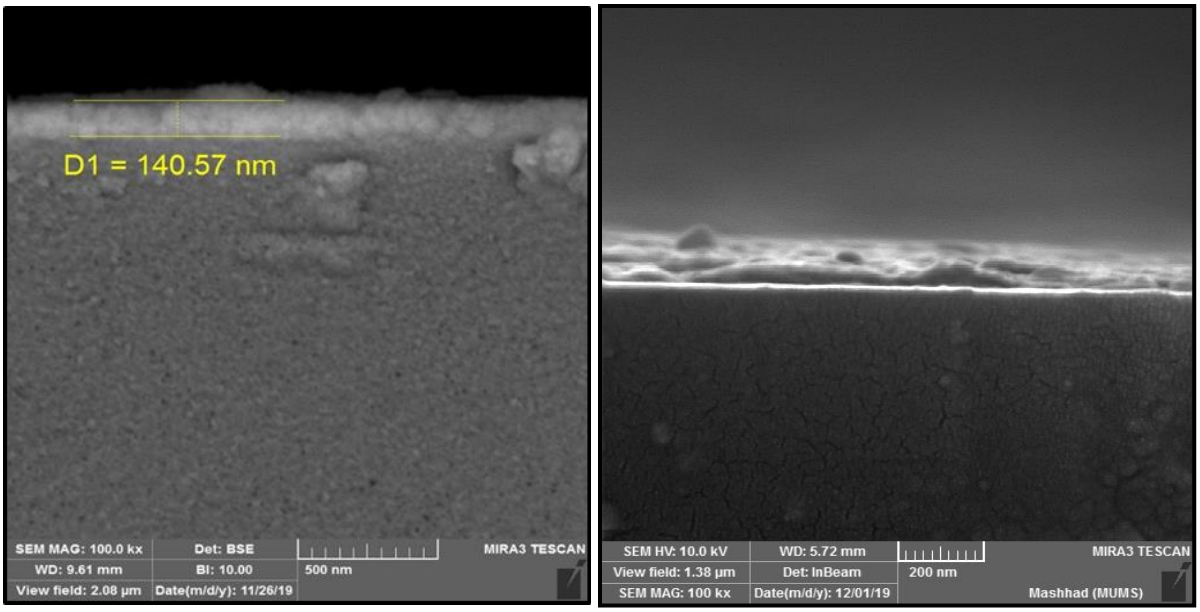

Figure 6: FESEM cross-section images of TiO2 and TiO2/GO thin films

4. Conclusion:

In this paper, structural and optical properties of TiO_2/GO heterostructures with different c by spin coating method are investigated. FESEM and AFM images also show that graphene oxide completely covers the titanium dioxide nanoparticles in the TiO_2/GO-4.5 sample.

The Raman spectra of the samples also shows the presence of D- and G-band at the wave numbers of 1350 Cm^{-1} and 1529 Cm^{-1} that are the characteristic of graphene oxide and confirm the presence of the sp^2 carbon structure. FTIR analysis of the samples showed that the Ti-O-Ti vibration peak is at the wavelength of 482 Cm^{-1} and with the addition of graphene oxide, the functional group peaks can be seen clearly. The presence of carbonyl and hydroxyl functional groups also confirms the presence of graphene oxide on the surface of TiO_2 thin film. Studying the absorption and transmission spectra of the samples shows that the addition of graphene oxide increases the absorption capacity of visible light in TiO_2 thin films. Optical band gap of TiO_2 with the addition of graphene oxide layer initially decreases, but by increasing the concentration of graphene oxide, the optical band gap increases to 2.9eV.

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