Preparation and investigation of optical properties and photocatalytic activity of SnO₂/GO thin films

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Abstract. In this study, tin oxide-pure (SnO₂) and tin oxide/Graphene Oxide (SnO₂/GO) thin films with different concentrations of GO (0, 1, 2, 3, and 4 g/ml) were synthesized using spin coating method. The synthesized thin films were used to study the structural, morphological, chemical, optical, and photocatalytic degradation of Methyl Orange (MO) under UV light irradiation using X-Ray Diffraction (XRD) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy, and Ultraviolet-Visible (UV-Vis) spectroscopy, respectively. The XRD results of GO showed that the peak was very sharp with high intensity, which was indicative of the quite good crystallinity of the GO structure. The band gap value of SnO₂/GO thin films increased followed by increase in the GO concentration. Under UV light irradiation, the photocatalytic activity of the synthesized samples was measured using MO dye. The obtained results also indicated that adding GO concentration would increase the photocatalytic activity of the SnO₂ thin film.

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1. Introduction

Semiconductors with the wide band gap ($E_g > 2.8$ eV) such as indium oxide, tin oxide (SnO₂), zinc oxide, and cadmium oxide have received considerable attention in recent years. These materials are characterized by a high intrinsic density of free charge carriers due to the deviation from the elemental proportion [1-4]. This deviation results from lack of oxygen in the crystalline lattice of these materials. In fact, while adding impurities, the free-charge density would be higher than the intrinsic density (close to the free carrier density of the metal). The electrical conductivity of these materials can be reduced through the impurity injection process, thus reaching the electrical conductivity of the conductors. These materials have been widely applied in technology and industry, e.g., in optoelectronic components (as transparent electrodes), automotive industries, airplanes (as transparent thermal elements), photovoltaic solar cell, and photo detectors (as anti-static coatings) [5-10].

SnO₂ is one of the important wide band gap semiconductors in technology used for a variety of applications in materials science and engineering. SnO₂ thin films are mainly known as transparent conductors whose electrical conductivity after doping them with donor atoms is quite large, i.e., in the order of $10^5$ S.cm⁻¹ [11-16]. In addition to SnO₂ high optical transparency in the visible region, it has been widely employed due to its mechanical stability, resistance to

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chemical corrosion, and low cost of pristine materials. This semiconductor material is characterized by an energy band gap ranging from 3.7 to 4.2 eV as well as a quadrilateral structure [17–19]. The first report on the preparation of SnO\textsubscript{2} transparent semiconductor layers in 2004 was attributed to the OGALE research group. The above-mentioned layers are characterized by a crystalline structure whose optical transparency in the visible region and carrier density are about 60\% and 10\textsuperscript{18} cm\textsuperscript{-3} [20], respectively. In recent years, with the growth of research interests in the transparent magnetic semiconductors field, researchers have studied the construction of transparent semiconducting magnetic SnO\textsubscript{2} with considerable impurities [21–23].

Another application of SnO\textsubscript{2} is the photocatalytic degradation of organic pollutants in the water and air, which has recently drawn the researchers' attention. Wang et al. studied the photocatalytic performance of ZnO/SnO\textsubscript{2} photocatalysts for Methyl Orange (MO) degradation [24]. They found that the photocatalytic activities of their samples reached the maximum value in case the Sn content and calcination temperature were about 33.3 mol\% and 500°C, respectively. Subramanian et al. synthesized CRGO and CRGO/SnO\textsubscript{2} nanocomposite for photocatalytic degradation of methylene green dye [25]. According to their obtained results, SnO\textsubscript{2}-C/annum Reduced Graphene Oxide (CRGO) nanocomposite exhibited a photodegradation efficiency rate of 97.4\%.

The results showed that Graphene-based semiconductor photocatalysts were well established for dye degradation applications in polluted water [25]. In this respect, the present study aimed to synthesize SnO\textsubscript{2}/GO thin films with different concentrations of GO (0, 1, 2, 3, and 4 g/ml) using spin coating method where all the reaction parameters were carefully optimized to retain the good crystalline structure of samples. To this end, the structural, morphological, chemical, and optical properties as well as photocatalytic degradation of MO under UV light irradiation of SnO\textsubscript{2}-pure and SnO\textsubscript{2}/GO thin films were carefully studied.

2. Experimental section

2.1. Preparation of SnO\textsubscript{2} thin layer

One gram of Tin Chloride was mixed with five cc of ethanol and stirred for 15 min. The solution was covered to rest for 24 hours under stirring. The glass substrates were rinsed using ultrasonic bath for 30 min at 60°C and then, they were placed in the acetone for 5 min and dried. The resulting solution was spin coated on the layers at a speed of 5000 rpm for 1 minute, and this process was repeated 50 times. The prepared layers were preheated for 20 min at 200°C and calcined for three hours at 500°C.

2.2. Preparation of Graphene Oxide (GO) thin layer

GO sheets were prepared from graphite using the Hummers method, as previously reported by researchers [26]. To prepare GO solution, 10 g, 20 g, 30 g, and 40 g of GO were solved in 10 cc of ethanol and dispersed in ultrasonic for 10 min. The GO solution was spin coated on SnO\textsubscript{2} layers at a speed of 5000 rpm for one min, and this process was repeated 25 times. To dry the layers, they were placed at 40–50°C for 30 min. These samples containing different concentrations of GO (0, 1, 2, 3, and 4 g/ml) were called SnO\textsubscript{2}-pure, SnO\textsubscript{2}/GO-10, SnO\textsubscript{2}/GO-20, SnO\textsubscript{2}/GO-30, and SnO\textsubscript{2}/GO-40, respectively. Then, characterization was performed on the samples.

3. Sample characterization

Through X-Ray Diffraction (XRD) method, the crystal structures of the prepared thin films were characterized by a D8 Advance Bruker YT diffractometer via Cu-K\alpha radiation in the range of 10"–80". The morphology of the layers was investigated using Field Emission Scanning Electron Microscopy (FESEM) performed on MIRRA3 TESCAN-XMU microscope. X-ray microanalysis system was supported by a Nano Trace LN-Cooled Si (Li) detector for Energy-Dispersive X-ray spectroscopy (EDX) analysis. Optical properties such as absorption and transmission spectra of the samples were studied using Ultraviolet-Visible (UV-Vis) device U3500 model. Room temperature Raman spectra were measured using micro-laser Raman spectrometer (Takram P500IR10) in backscattering configuration, employing the 532 nm line of Nd:YAG laser as the excitation source.

4. Result and discussion

4.1. Structural properties

The crystalline structures of SnO\textsubscript{2}-pure, SnO\textsubscript{2}/GO-10, SnO\textsubscript{2}/GO-20, SnO\textsubscript{2}/GO-30, and SnO\textsubscript{2}/GO-40 thin films with different concentrations of GO were recorded by XRD in the range of 2θ = 10 – 80° using Cu-K\alpha radiation, the results of which are reported in Figure 1. Figure 1(a) shows the pure sample which confirms the formation of a crystalline structure without any additional peaks. In addition, SnO\textsubscript{2} peaks are located at 2θ = 26.5, 33.8, 37.9, and 51.7°, which correspond to (110), (101), (200), and (211) reflecting planes, respectively. According to the JCPDS (41–1445) card number, the pure sample is characterized by the casseriterite phase [27]. Figure 1(b)–(e) show the SnO\textsubscript{2}-GO samples with different GO concentrations. According to these figures, compared to SnO\textsubscript{2} peaks, the GO peak intensity at an angle of 10° is quite high, thus confirming the presence of GO in samples. The
peaks are quite sharp with high intensity, indicating good crystallinity of the GO structure. No additional peaks are observed in these figures. According to Scherrer equation, the average grain sizes of pure SnO\(_2\), SnO\(_2\)/GO-10, SnO\(_2\)/GO-20, SnO\(_2\)/GO-30, and SnO\(_2\)/GO-40 thin films are 57, 70, 67, 65, and 60 nm, respectively, all in the nanometer range, resulting in significant dispersion across the grain boundaries. Hence, its mobility is low and we expect the resistivity of the layers to be high. The lattice parameter values of SnO\(_2\)-pure thin film are \(a = 4.722\) Å, \(b = 5.753\) Å, and \(c = 5.245\) Å, respectively, all in good agreement with the results reported by other researchers [28, 29].

4.2. Morphological analysis using FESEM, cross-sectional, and EDX

Microstructure and surface morphology of SnO\(_2\)-pure, SnO\(_2\)/GO-10, and SnO\(_2\)/GO-40 thin layers were characterized by FESEM images. FESEM results of these samples are shown in Figure 2. Figure 2(a) shows a

![Image of X-Ray Diffraction (XRD) patterns](image)

**Figure 1.** X-Ray Diffraction (XRD) patterns of (a) SnO\(_2\)-pure, (b) SnO\(_2\)/GO-10, (c) SnO\(_2\)/GO-20, (d) SnO\(_2\)/GO-30, and (e) SnO\(_2\)/GO-40 thin films.

![Image of Field Emission Scanning Electron Microscopy (FESEM) images](image)

**Figure 2.** Field Emission Scanning Electron Microscopy (FESEM) images of (a) SnO\(_2\)-pure, (b) SnO\(_2\)/GO-10, and (c) SnO\(_2\)/GO-40 thin films.
SnO₂-pure sample whose surface is completely uniform and smooth with a quite small size of grains, i.e., less than 100 nm. In SnO₂/GO-10 and SnO₂/GO-40 samples (Figure 2(b) and (c)), the GO plates are clearly shown to be overlapping together and covering the SnO₂ surface. The cross-sectional images of SnO₂-pure and SnO₂/GO samples are shown in Figure 3. According to the pure sample, the surface of the sample is quite uniform (with a thickness of 350 nm); however, after adding GO, the layer surface becomes completely rough (with a thickness of 570 nm). Characterized by wrinkled structures, GO sheets overlap each other, as shown in Figure 2(b) and (c). Hence, upon adding GO, plates can increase the thickness and surface roughness of the layers. To determine the composition type of the synthesized layers, EDX analysis was employed. Figure 4 illustrates the obtained results for SnO₂-pure layers in the presence of GO with concentrations of 1 and 4 g/ml. While Figure 4(a) presents the Sn- and O-related peaks only, Figure 4(b) and (c) show the carbon-related peaks that confirm the presence of GO in these structures.

4.3. **Chemical properties: Raman spectroscopy**

Raman spectroscopy is a non-destructive technique that is employed to obtain structural information about samples, especially about carbon structures. Figure 5 demonstrates the Raman spectra of SnO₂-pure, SnO₂/GO-10, and SnO₂/GO-40 thin films with different GO concentrations prepared by spin coating method. The main characteristic of the samples

![Figure 3](image3.png)

**Figure 3.** Cross-section of (a) SnO₂-pure and (b) SnO₂/GO-40 thin films.

![Figure 4](image4.png)

**Figure 4.** Energy Dispersive X-ray spectroscopy (EDX) analysis of (a) SnO₂-pure, (b) SnO₂/GO-10, and (c) SnO₂/GO-40 thin films.

![Figure 5](image5.png)

**Figure 5.** Raman spectra of (a) SnO₂-pure, (b) SnO₂/GO-10, and (c) SnO₂/GO-40 thin films.
containing carbon in their structure is the presence of the G and D peaks that are indicative of the sp² carbon fluctuations arranged at the wavelengths of about 1580 cm⁻¹ and 1350 cm⁻¹, respectively. Generally, the intensity of D peak is used to determine the disorder degree of the structure. According to the picture, the intensity of D peak is higher than that of G peak. Hence, the structure is very disorderly [30,31].

4.4. Optical properties
To confirm the capabilities of the optical properties of SnO₂-pure, SnO₂/GO-10, SnO₂/GO-20, SnO₂/GO-30, and SnO₂/GO-40 thin films with different GO concentrations, UV-Vis absorption spectroscopy was employed. UV-Vis absorption spectra of SnO₂/GO thin films were measured at a wavelength ranging from 250 to 900 nm. Figure 6 presents the UV-Vis absorption spectra of the synthesized thin films. The edge absorption for SnO₂/GO-40 thin films was detected at 380 nm. For GO, red shift occurred in the range of 310 nm to 370 nm after the reduction of GO to rGO. A peak was observed with maximum absorption at 310 nm and the other neighboring high absorption peaks were also seen for SnO₂/GO thin films with different concentrations and a noticeable red shift in maximum absorption. This red shift occurred mainly due to the presence of semiconductor SnO₂ nanoparticles on the graphene sheet. Interestingly, in the case of SnO₂/G nanocomposites, the peak observed at 310 nm was associated with the graphene red-shifts at 340 nm, indicating an increase in the π-electron concentration followed by the reduction of sp³ GO to sp²-hybridization of carbon atoms [32]. The absorption edge red shift was observed at the higher energy band > 3.0 eV. The red shift in the band gap was observed due to the improved crystallinity of the thin film. The optical band gap of the film decreases with an increase in the grain size. The barrier height of the grain boundary increased with an increase in the grain size, thus resulting in a decrease in the band gap of the thin film. Through this test, it was found that the samples had good absorption in the visible light or UV range.

The spectral distributions of transmittance of SnO₂-pure, SnO₂/GO-10, SnO₂/GO-20, SnO₂/GO-30, and SnO₂/GO-40 thin films with different GO concentrations were evaluated with normal occurrence in the wavelength range of 250-900 nm, the results of which are shown in Figure 7. According to this figure, SnO₂-pure thin films exhibit high transmittance ranging from 70% to 90%. In the case of adding 10, 20, 30 g of GO, the transmittance would decrease. Further, upon increasing the concentration of GO up to 40, its transmittance would increase more than that of the pure sample. This finding may be attributed to the decrease in the grain size of these films, as was demonstrated by the calculations of the Scherrer relation in the XRD section with the increasing concentrations of GO.

From the transmittance spectra, the optical band gap energy of SnO₂/GO thin films can be calculated using Tauc's relation [33,34]:

\[(\alpha h\nu)^{1/n} = A(h\nu - E_g)\],

where \(h\nu\) is the photon energy, \(\alpha\) the absorption coefficient, \(A\) the constant, and \(E_g\) the band gap of the material. The exponent \(n\) depends on the type of the transition: for direct and allowed transition, \(n = 1/2\); for indirect transition, \(n = 2\); and for direct un-allowed transition, \(n = 3/2\).

In order to calculate the direct band gap value, \((\alpha h\nu)^2\) versus \(h\nu\) was plotted, as shown in Figure 8. The band gap value can be measured using the straight portion of the graph on \(h\nu\) axis at \(\alpha = 0\).
The band gap value for SnO$_2$-pure is 3.56 eV, and the values for SnO$_2$/GO-10, SnO$_2$/GO-20, SnO$_2$/GO-30, and SnO$_2$/GO-40 are 3.65 eV, 3.7 eV, 3.8 eV and 3.9 eV, respectively. The band gap value for the thin films increased upon increasing the GO concentration, mainly due to decrease in the GO grain size resulting from nano-scale electron confinement, called “quantum size effect”. In other words, electron is confined which in turn occupies less space than bulk; therefore, Valence Band Maximum (VBM) and Conduction Band Minimum (CBM) potentials are shifted more to + eV and − eV, respectively, causing a wider band gap. These results are in agreement with those reported in other studies [35]. The band gap of pure SnO$_2$ thin film was reported to be 3.42 eV in the study of Camacho-López et al., which increased up to 3.69 eV upon increasing the substrate temperature from 50 to 250°C [36]. Moreover, Soumia and Nasr-Eddine calculated the band gap of SnO$_2$ thin film as 3.6 eV [37].

4.5. Photocatalytic activity
Under UV light irradiation, the photocatalytic activity of synthesized samples was measured using MO dye as the typical organic pollutant in water. Figure 9(a)–(c) demonstrate the UV-Vis absorption spectra of SnO$_2$-pure, SnO$_2$/GO-20, and SnO$_2$/GO-40 thin films with adsorbed MO in 60 min. First, 30 cc of 10 ppm of MO solution was put in a dark environment for 30 min to reach the absorption-desorption balance (sample $A_0$). The solutions were then irradiated by two UVC (200–250 nm) and UVB (280–315 nm) lamps of 18 W for 60 min (sample $A_t$). The percentage of MO degradation with absorption measurement in the wavelength of 464 nm was calculated through the following equation:

$$\frac{A_0 - A_t}{A_0} \times 100.$$  

(2)

SnO$_2$-pure thin film did not exhibit the degradation efficiency under UV light irradiation for the 60 min time duration (Figure 9(a)). The degradation efficiency of SnO$_2$/GO-20 and SnO$_2$/GO-40 thin films was 2.2 and 3.4%, respectively. By adding GO concentration, the photocatalytic activity of the SnO$_2$ thin film increased. The presence of GO plates provided extra trapping sites for incoming photo-generated charge carriers, which resulted in better photocatalytic activity [38]. Karimabad et al. [39] investigated the photocatalytic activity of SnO$_2$ nanoparticles in the presence of MO. Their results indicated that as the time increased, the peak intensity decreased and it would disappear completely after 60 min (about 80–90% degradation). By comparing our results with those of Soumia and Nasr-Eddine [37], it seems that SnO$_2$ nanopowder has better photocatalytic properties than its thin film. Given the active surface area of the thin films was smaller than the nanopowder, the decomposition rate was much lower and the photocatalytic property of thin films was less than nanopowder. Similar results were also reported by researchers for other materials such as TiO$_2$ [40].

5. Conclusion
In this study, SnO$_2$-pure, SnO$_2$/GO-10, SnO$_2$/GO-20, SnO$_2$/GO-30, and SnO$_2$/GO-40 thin films with different Graphene Oxide (GO) concentrations were synthesized using spin coating method. The structural,
morphological, chemical, optical, and photocatalytic
degradations of Methyl Orange (MO) under UV light
irradiation were also studied. The X-Ray Diffraction
(XRD) results showed that the peaks were quite sharp
with very high intensity, indicating the good crys-
tallinity of the GO structure. No additional peaks
were observed. Field Emission Scanning Electron
Microscopy (FESEM) images revealed that the surface
of the pure sample was completely uniform and smooth
and the size of the grains was very small, i.e., less
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of SnO2. G and D peaks were indicative of the
presence of GO arranged at the wavelengths of about
1580 cm⁻¹ and 1350 cm⁻¹, respectively. The band
gap value of SnO2-pure was 3.56 eV which increased
by increasing the GO concentration. The band gap
value of the thin films also increased followed by an
increase in the GO concentration. An increase in the
band gap value led to an increase in the concentra-
tion that in turn resulted from a decrease in the particle
size. Under UV light irradiation, the photocatalytic
activity of the synthesized samples was measured using
MO dye. Degradation efficiencies of SnO2/GO-20 and
SnO2/GO-40 thin films were measured as 2.2 and 3.4%,
respectively. The MO adsorption was completed on the
surfaces of both GO and metal oxides using the
prepared thin films.

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**Biographies**

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