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Plasma physics impact on energy and environmental-synthesis and characterization of rGO/CoSnO₃ for energy and environmental remediation

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Abstract

Graphene oxide was reduced and wrapped around cobalt tin oxide nanoparticles using a simple hydrothermal process. The rGO/CoSnO₃ nanocomposite was analyzed using analytical techniques including TG-DTA, XRD, FT-IR, SEM with EDS, XPS, and UV-DRS. TG-DTA analysis verified the melting point and phase transition at a specific calcination temperature. The phase and crystalline size of graphene oxide (GO), reduced graphene oxide (rGO), cobalt oxide (Co₃O₄), cobalt stannate (CoSnO₃), and rGO/CoSnO₃ are 19.8 nm, 27.6 nm, 26.9 nm, 40.3 nm, and 50.4 nm, respectively. XPS analysis was utilized to investigate the elemental composition and ionic state. The SEM analysis showed that CoSnO₃ agglomerated nanoparticles are evenly spread across the surface of rGO, forming a 2D sheet structure. The band gap of rGO, Co₃O₄, CoSnO₃, and rGO/CoSnO₃ was determined by UV-DRS examination and Kubelka-Munk function diagram analysis, revealing values of 3.5, 2.4, 4.5, 2.7, and 1.6 eV, respectively. We used methylene blue dye for photocatalytic degradation with GO/CoSnO₃ nanocomposite and attained a degradation efficiency of 96.2%. The CoSnO₃ and rGO/CoSnO₃ nanocomposites are utilized as electrode materials in three-electrode and symmetric electrochemical supercapacitors. Electrochemical study shows that CoSnO₃ and rGO/CoSnO₃ electrodes have high supercapacitance values of 158.8 F/g and 499.7 F/g at a scan rate of 10 mV/s, respectively. The charge-discharge curves of the rGO/CoSnO₃ electrode indicated a specific capacitance of 603.12 F/g at 1 A/g, which was higher than the specific capacitance of the CoSnO₃ electrode, which was 285.3 F/g at 1 A/g. The rGO/CoSnO₃ electrode has a cyclic performance where it maintains 96.2% capacity retention even after 1000 cycles. This research finding could be valuable for mitigating water contamination and utilized as a supercapacitor material.

Keywords: Plasma physics, cobalt oxide, hydrothermal, photocatalytic degradation, methylene blue, cyclic voltammetry

1. Introduction

Environmental contamination has become a significant issue in recent years. Pollutants are steadily rising, leading to significant and irreversible harm to the Earth's environment. Industrial effluents are recognized as the primary cause of water pollution [1-3]. Photocatalytic degradation is a crucial method for treating wastewater by removing toxic heavy organic pollutants. Traditional wastewater treatment procedures have secondary impacts such as high separation costs as well as the production of second-order contaminants through processes including adsorption, coagulation, as well as membrane dissociation, which incur substantial operational expenses. Graphene is considered a viable support material for energy storage batteries due to its ability to enhance charge transfer and mass transport. Graphene oxide also exhibits increased photocatalytic degradation properties. CoSnO₃ is a semiconductor compound made of transition metals with a wide-direct band gap. CoSnO₃ nanostructures have garnered significant interest for their prospective applications in domains for instance, photocatalytic activity, gas sensors, glucose sensors, and solar cells. Metal oxides typically exhibit superior photocatalytic effectiveness [9, 10]. rGO/CoSnO₃ is the most effective photocatalyst due to its exceptional stability. The development of a novel and efficient nanocomposite is increasingly important since it is an ecologically friendly product. Co₃O₄, CoSnO₃, and rGO/CoSnO₃ were utilized to assess Methylene blue dye's deterioration in the presence of sunlight and UV light exposure, and the results were examined and analyzed.

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2. Experimental setup

2.1 Materials

The investigation utilized Graphite powder, potassium permanganate, sulfuric acid, and sodium nitrate, Tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Oxalic acid, and Hydrogen peroxide in their analytical grade without additional purification.

2.2 Synthesis of Graphene Oxide

Graphene Oxide was produced using a modified version of the Hummer's process. 46ml of sulfuric acid, 1g of graphite powder, and sodium nitrate were combined in a beaker and stirred at 500 rpm for one hour. 6 grams of KMnO_4 was added gradually to the solution and left to stir for 30 minutes in an ice bath at 37 °C. Additionally, 50ml of water was added slowly, and the mixture was cooled to ambient temperature before being heated to 100 °C. Subsequently, 10ml of H_2O_2 was added to facilitate the synthesis of graphene oxide [15].

2.3 Synthesis of Reduced Graphene Oxide

400 mg of powdered graphene oxide (0.1 mg/mL) was dissolved in 20 ml of water. Then, 10 ml of hydrogen hydrate was added as a reducing agent to decrease the graphene oxide. The mixture underwent centrifugation at a speed of 4000 revolutions per second for 40 minutes following 30 minutes of stirring on a magnetic stirrer at a temperature of 60 °C. The mixture was rinsed with ethanol and distilled water, then dried at 120 °C for 24 hours.

2.4 Synthesis of Cobalt Oxide

Cobalt oxide is frequently produced by the hydrothermal technique in a standard synthesis process. 1.6 grams of cobalt chloride hexahydrate and 0.6 grams of oxalic acid were dissolved in 70 milliliters of water. The mixture was continuously whirled for 30 minutes at room temperature. The mixture was placed in a Teflon-lined stainless steel autoclave and maintained at a temperature of 120 °C for a duration of 12 hours. The product was washed with water and ethanol to remove impurities then dehydrated at 80 °C using air cooling. The material was annealed at 400 °C for 5 hours in a muffle furnace [18].

2.5 Synthesis of Cobalt Tin Oxide

1.6 grams of cobalt chloride dihydrate and 0.6 grams of oxalic acid were dissolved in water. 0.9 grams of tin(II) chloride dihydrate was added gradually. The solution was agitated incessantly for 30 minutes at room temperature. The blend

was placed in a Teflon-coated stainless steel autoclave and maintained at 120 °C for 12 hours. The product was washed with water and ethanol to remove any remaining ions, then dried at 80 °C in the atmosphere. The powder underwent annealing at 450 °C for 5 hours in a muffle furnace [19].

2.6 Synthesis of rGO/CoSnO₃ Nanocomposite

30 mg of reduced graphene oxide (rGO) was sonicated for 10 minutes with the gradual addition of 1.6 g of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, 0.9 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and 0.6 g of oxalic acid. The solution was agitated consistently for 30 minutes at ambient temperature. The mixture was placed in a Teflon-lined stainless steel autoclave and kept at 120 °C for 12 hours. The final product was cleaned with ethanol and water, dried at 80 °C, and then heated at 450 °C for 5 hours in a muffle furnace.

3. Results and Discussion

3.1 Thermal Gravimetric - Differential Thermal Analysis (TG-DTA)

The thermal stability of produced Co_3O_4 and CoSnO_3 nanoparticles was examined by TG-DTA analysis. The nanomaterials were heated from room temperature to 1100 °C at a rate of 20 °C per minute in an air environment. DTA techniques were used to study the thermal properties of produced $\text{Co}(\text{OH})_2$ nanoparticles. $\text{Co}(\text{OH})_2$ experienced thermal decomposition in three stages. The initial weight loss from room temperature to 130 °C was caused by the removal of free water through dehydration and evaporation, leading to a 14% decrease in weight [22]. A second weight loss occurs between 130 °C and 230 °C, with around 15% of unnecessary moisture being lost. The third weight loss occurs at approximately 28% between 230 °C and 700 °C. At temperatures exceeding 700 °C, Co_3O_4 is formed and remains stable without any loss of mass, demonstrating the thermal stability of the crystalline Co_3O_4 sample. The exothermic peak about 700 °C was clearly observed due to the decalescence phenomenon, likely caused by the transition from the amorphous to the crystalline phase. Figure 1 shows the TG-DTA curve of $\text{CoSn}(\text{OH})_2$ [23]. The initial weight loss occurs at 160 °C, representing approximately 22% of the total weight loss, which is attributed to dehydration and the elimination of free water from the initial precursor. At 850 °C, an extra 43% weight loss occurs as a result of the dehydration of $\text{CoSn}(\text{OH})_2$. The calcination temperature of $\text{CoSn}(\text{OH})_2$ is determined to be 500 °C based on TG-DTA analysis [26-27]. The TGA study has verified the necessary temperature range for the CoSnO_3 nanocomposite that was synthesized.

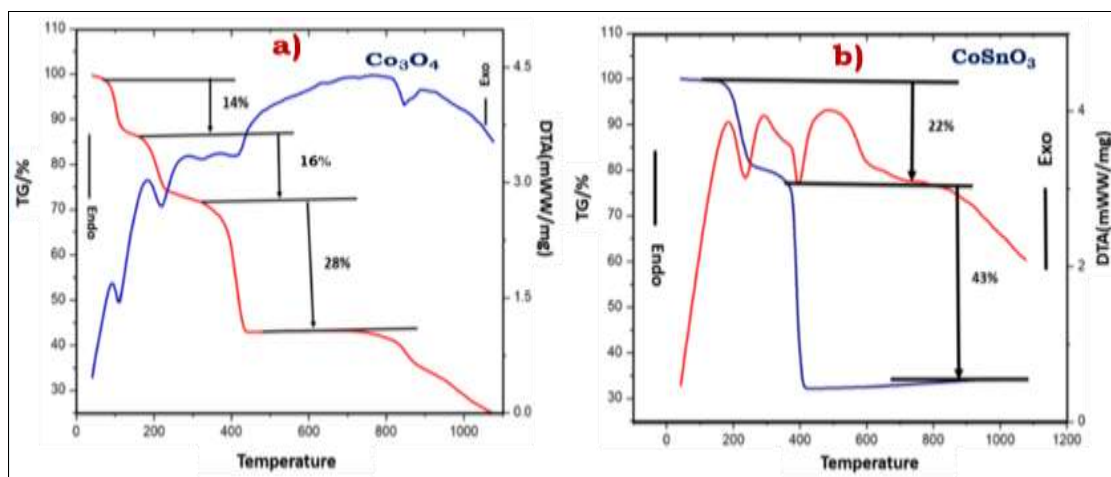


Fig 1: TG-DTA Analysis of (a) CoSnO_3 and (b) rGO/CoSnO₃ nanocomposites

3.2 XRD Analysis

The TG-DTA analysis showed the presence of CoSnO_3 and rGO/ CoSnO_3 nanocomposite. The X-ray diffraction (XRD) patterns of the samples, post-calcination at 500 °C, revealed diffraction peaks at 2θ values corresponding to the planes (220), (422), and (511) of Co_3O_4 nanoparticles, as per JCPDS Card No. 42-1467 [28]. The CoSnO_3 composite exhibits reflections on the planes (211), (220), (400), (422), and (511),

which correspond well with JCPDS Card No. 29-0514 [29-30]. The CoSnO_3 nanoparticle production started at around 450 °C during calcination [30]. No peaks are observed in other phases, demonstrating the excellent purity of the compounds depicted in (Fig.2). The various characteristics, including the crystallite size of the rGO/ CoSnO_3 nanocomposite, are determined using the Debye–Scherrer formula (Equation 1) and are listed in Table 1 [31].

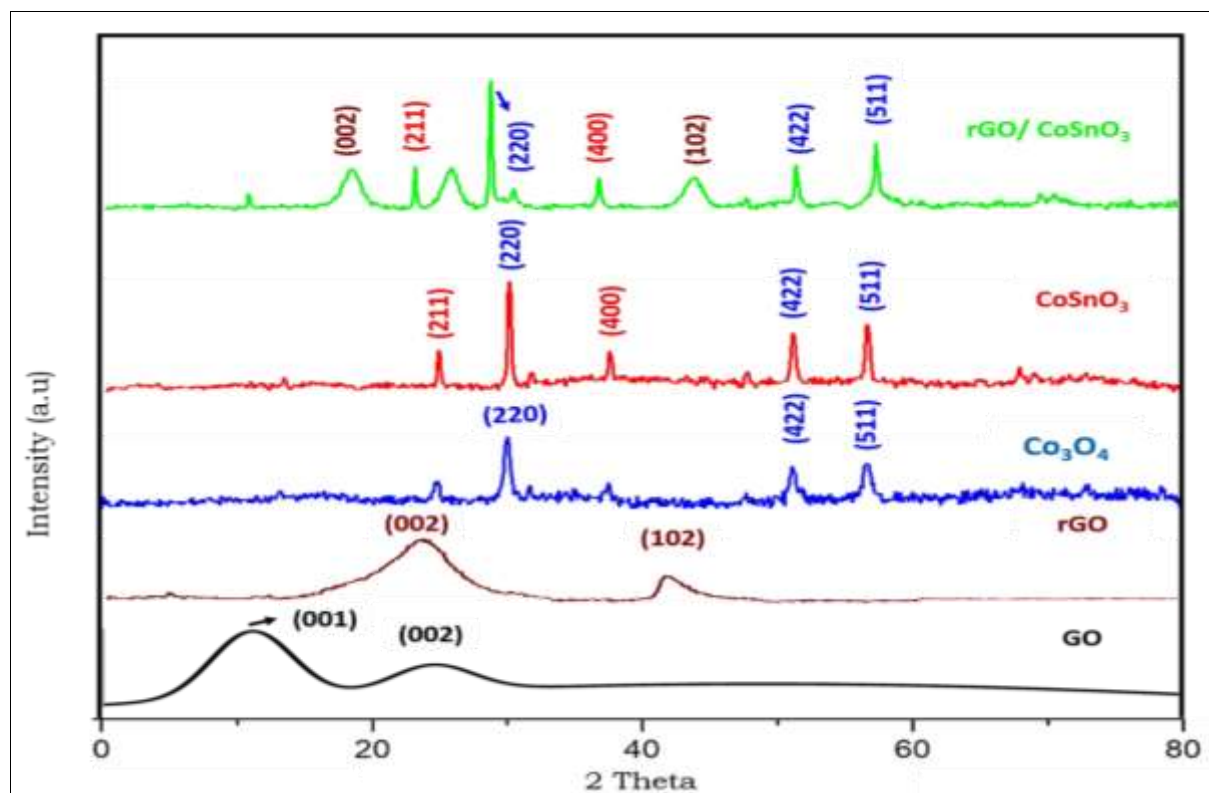


Fig 2: XRD spectra of (a) GO, (b) rGO, (c) Co_3O_4 , (d) CoSnO_3 and (e) rGO/ CoSnO_3

3.2.1 Debye–Scherrer's equation

$$\text{Crystalline size (D)} = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the wavelength ($\lambda = 1.5406 \text{ \AA}$ (Cu $K\alpha$)), β is the full width half maximum (FWHM) and θ is the diffraction angle.

Table 1: Crystalline size of Co_3O_4 , CoSnO_3 and rGO/ CoSnO_3 nanocomposite

S. No	Sample	Crystalline Size(nm)
1.	GO	19.8
2.	rGO	27.6
3.	Co_3O_4	26.9
4.	CoSnO_3	40.3
5.	rGO/ CoSnO_3	50.4

3.3 FT-IR Spectrum of rGO/ CoSnO_3 Nanocomposite

FT-IR is a powerful method for analyzing the many functional groups present in graphene oxide, particularly those related to oxygen. The FT-IR spectra of GO in Fig.3 confirmed the successful oxidation of the graphite. Figure 3b displays absorption stretching vibration peaks at 1099 cm^{-1} and 1623 cm^{-1} , corresponding to the stretching of C-O and C=O groups. Additionally, the vibration band at 1392 cm^{-1} is attributed to the stretching mode of the H-O-H group in rGO. The peaks at 566 cm^{-1} and 665 cm^{-1} correspond to the stretching vibrations of the Co-O bond in Figure 3c. The pure CoSnO_3 exhibited distinctive bands, notably the H-O-H bond at 3419 cm^{-1} as shown in Fig.3d, which align well with previously published values. The band at 540 cm^{-1} in the rGO/ CoSnO_3 composite is attributed to the metal-oxygen stretching vibration. This co-existence is important as it hinders the recombination of charge carriers and boosts the supercapacitor and catalytic properties of the nanocomposite through a synergistic effect.

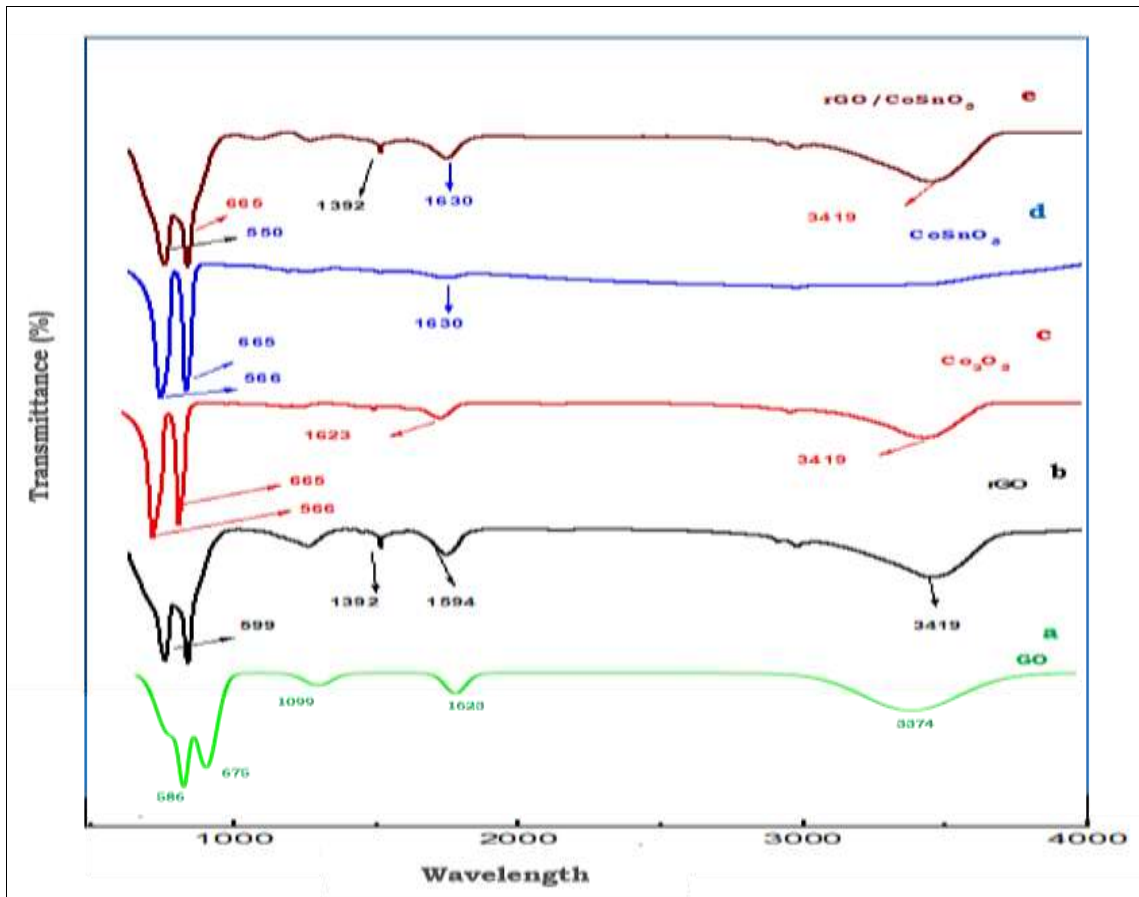
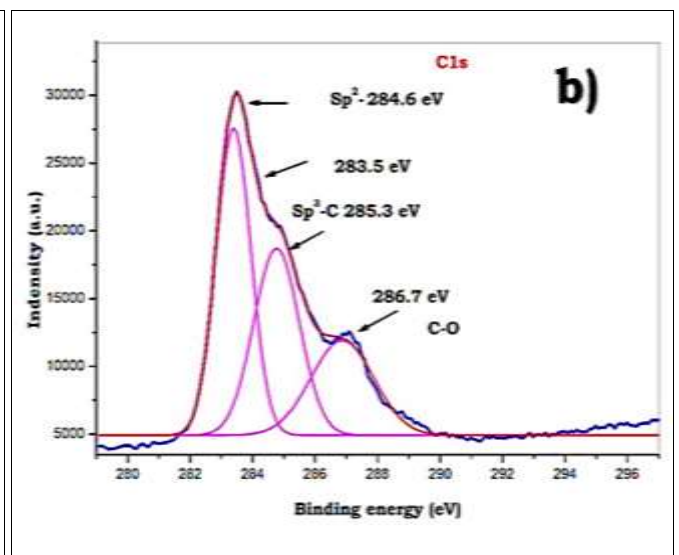
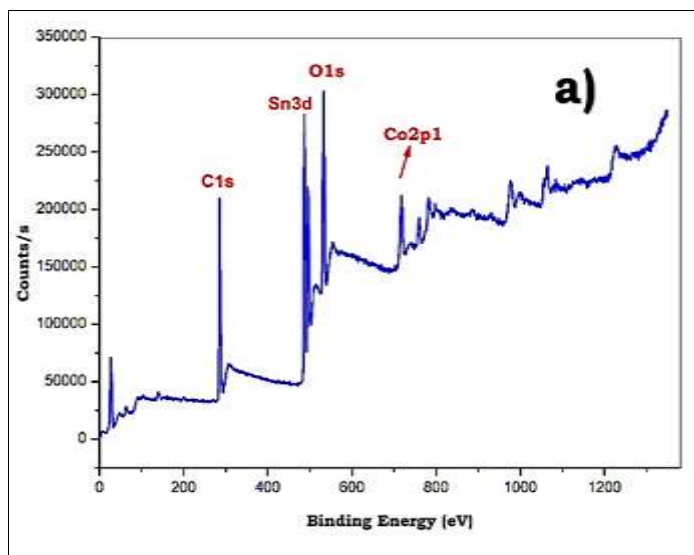


Fig 3: FT-IR Spectrum of (a) GO, (b) rGO, (c) Co₃O₄, (d) CoSnO₃ and (e) rGO/CoSnO₃

3.4 XPS analysis

The elemental composition and chemical state of prepared nanocomposite confirmed by X-Ray Photoelectron Spectroscopy. The XPS spectra Fig.4a shows that the existence of Sn, Co, O and C elements in composite. Fig.4b show the C1s and the Co₃O₄ binding energy observed at 781.7eV corresponding to Co2p^{1/2} respectively (Fig.4c). Fig.4d

display the high resolution spectrum of Sn 3d where binding energy at 495.3 and 486.7 eV characteristic of 3d^{3/2} and 3d^{5/2}, respectively which is in agreement with Sn²⁺ state. The XPS spectra of Co 2p shows in fig.2b, Co 2p binding energy procured at 781.7 eV and O1s having 532 eV binding energy (Fig.4e). With the aforementioned results would suggest that purity of the synthesized nanocomposite.



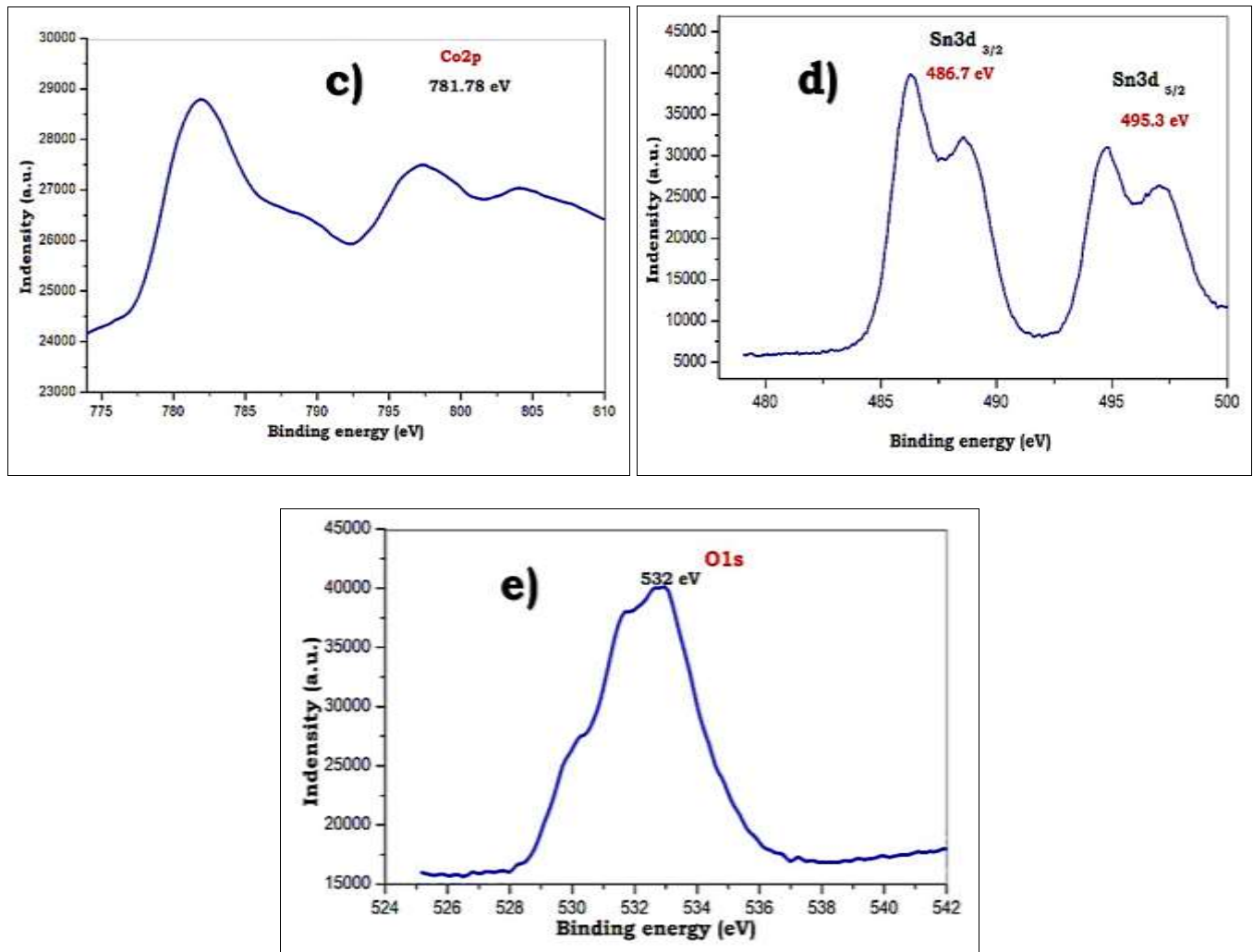


Fig 4: XPS Spectra of rGO/CoSnO₃ a) survey spectrum, b) C1s spectrum, c) Co2p spectrum, d)Sn3d spectrum and e) O1s spectrum

3.5 Correlation of Photocatalytic Activity with Band Structure

Using a catalyst and an irradiation source, photocatalysis accelerates a photoreaction. Free radicals like hydroxyl radicals (•OH) are the driving force behind photocatalysis processes, and the capacity of the catalyst to produce electron-hole pairs is critical. As the photocatalyst's optical sensitivity shifts to longer excitation wavelengths, its band gap energy decreases. Photocatalyst band gaps may be reduced using a variety of techniques. Band gap is inversely proportional to catalytic activity (equ-4). The rGO/CoSnO₃ has the lowest band gap energy value (1.6 eV) compared to bare materials (Co₃O₄ = 4.5eV, CoSnO₃ = 2.7eV) hence the material exhibited a high Photocatalytic property.

$$\text{Band gap} \propto \frac{1}{\text{Catalytic Property}} \quad (4)$$

S. No	Sample	Band gap (eV)	Degradation percentage (%)	
			Sunlight	UV-Light
1.	Co ₃ O ₄	4.5	83.6%	62.0%
2.	CoSnO ₃	2.7	85.8%	72.0%
3.	rGO/CoSnO ₃	1.6	96.2%	75.2%

3.6 Correlation of Photocatalytic Activity with crystallite size

For this work, micrometer-sized particles were used to reduce the influence of other catalytic characteristics (such as

excessive surface area and quantum confinement effect) on photocatalytic experiments.

In continuous process conditions, the findings showed that the photocatalytic capabilities were highly reliant on the crystallinity of the material. Increases in crystallite size have a significant impact on the accelerated photodecomposition of organic matter. The propensity for crystallite size to have an effect was further demonstrated by altering the quantity of catalysts in the photocatalytic reaction. The rGO/CoSnO₃ nanocomposite having a larger particle size (50.4nm) compared to bare materials (Co₃O₄ = 26.9 and CoSnO₃ = 40.3) inferred that the nanocomposite of rGO/CoSnO₃ was easily degrading the dye molecules.

$$\text{Crystalline size} \propto \text{Catalytic Property} \quad (5)$$

S. No	Sample	Crystalline Size (nm)	Degradation percentage (%)	
			Sunlight	UV-Light
1.	Co ₃ O ₄	26.9	83.6%	62.0%
2.	CoSnO ₃	40.3	85.8%	72.0%
3.	rGO/CoSnO ₃	50.4	96.2%	75.2%

3.7 Morphology Analysis

SEM micrographs were used to study the surface morphology of the prepared rGO, Co₃O₄, CoSnO₃, and rGO/ CoSnO₃. The SEM pictures in Fig.5.a-e reveal that GO and rGO had a sheet-like structure. The CoSnO₃ nanoparticle appeared in an agglomerated form. Figure 5c displays the cubic surface

morphology of Co_3O_4 . The rGO/ CoSnO_3 nanocomposite exhibited CoSnO_3 nanoparticles in a cubic form scattered

across the rGO surface in various orientations.

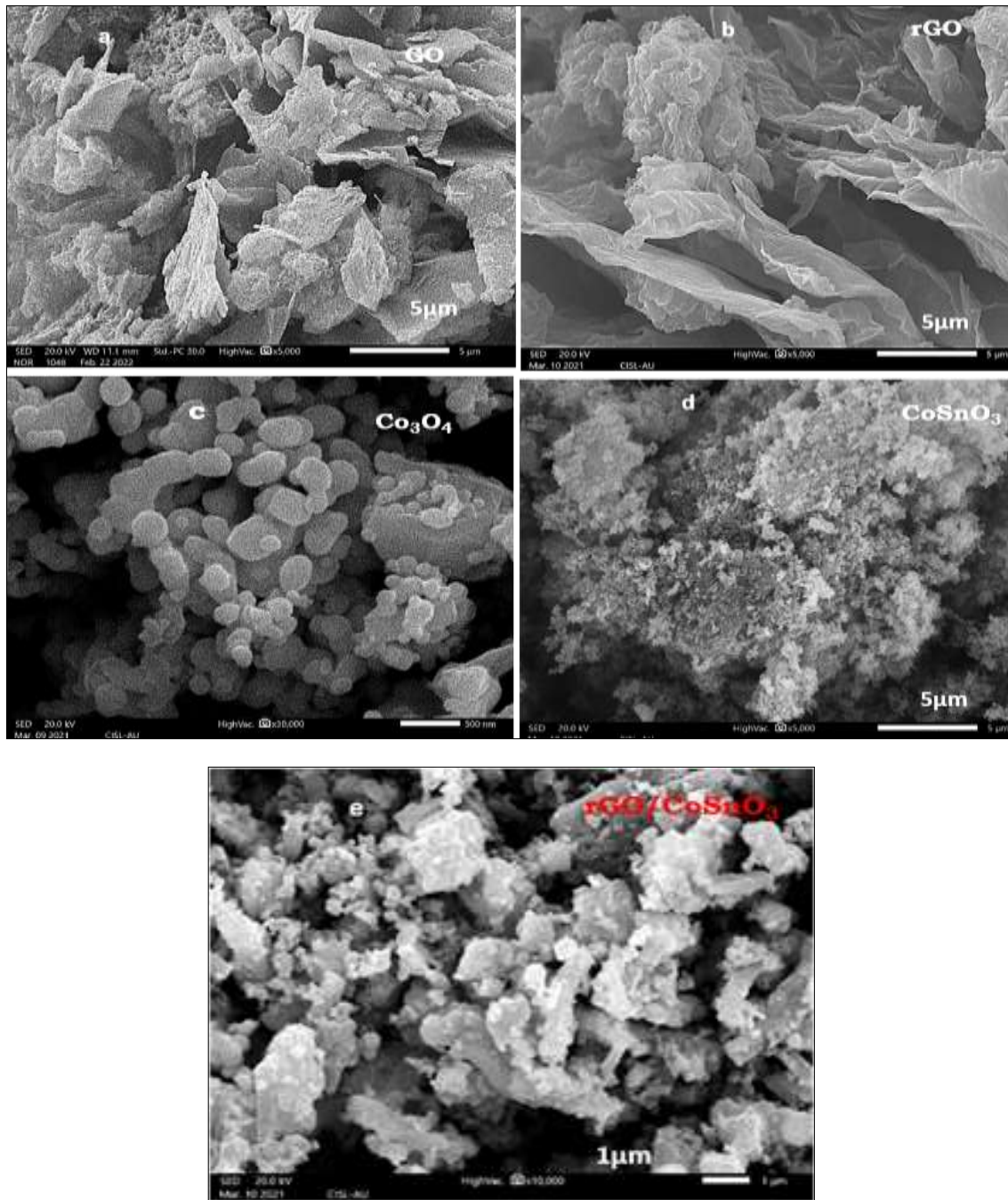


Fig 5: SEM analysis of GO, rGO, Co_3O_4 , CoSnO_3 and rGO/ CoSnO_3

3.8 EDX Analysis of rGO, Co_3O_4 , CoSnO_3 and rGO/ CoSnO_3 nanocomposite

The EDX analysis was used to interpret the elemental and chemical composition of the prepared nanocomposite. The EDX spectrum of rGO, Co_3O_4 , CoSnO_3 , rGO/ CoSnO_3 nanocomposite revealed a homogeneous distribution of C, O,

Co and Sn in the rGO/ CoSnO_3 composite. The percentage of C, O, Co and Sn in the nano material was carried out according to the EDX analysis (Fig.6). The quantitative analysis of EDX revealed that the atomic ratio of Co: Sn was 1:3.

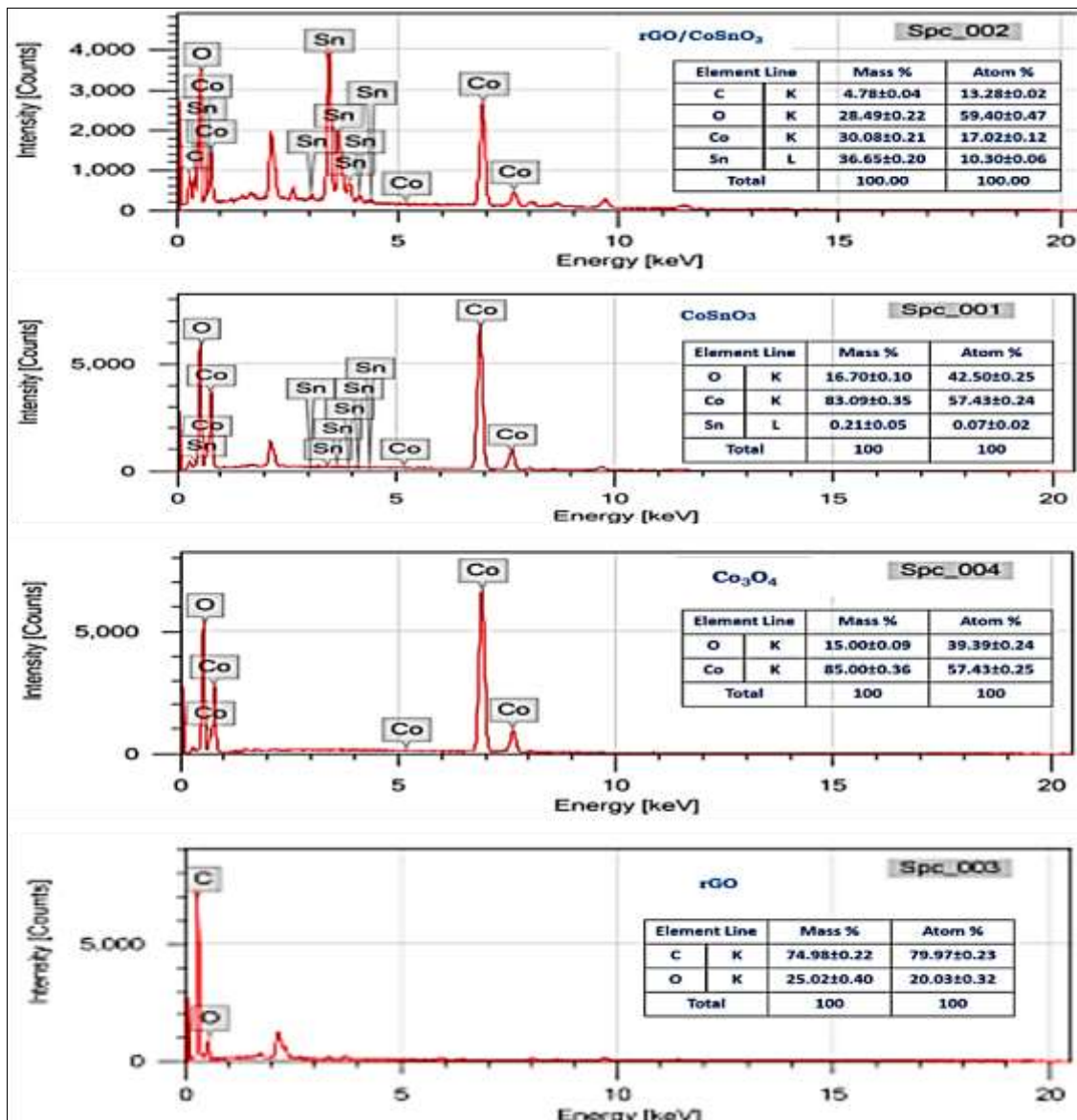
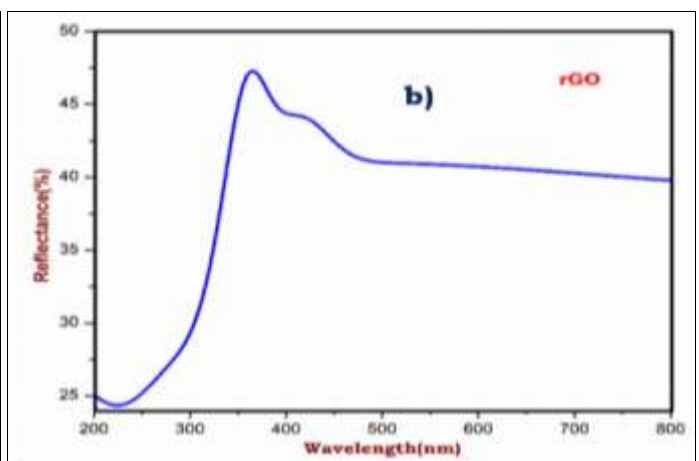
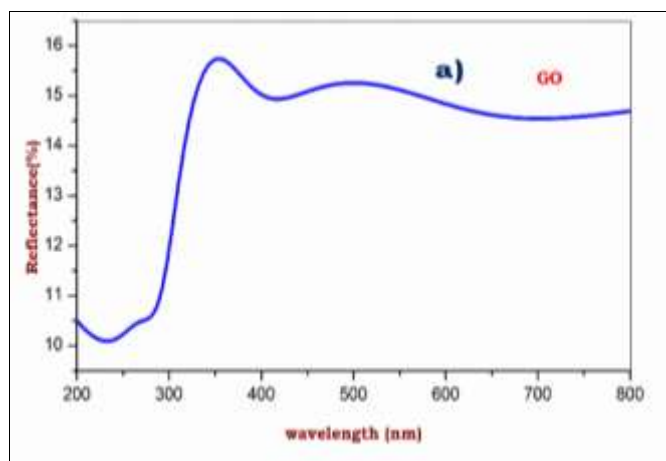


Fig 6: EDS analysis of rGO, Co₃O₄, CoSnO₃ and rGO/CoSnO₃

3.9 UV - DRS Analysis

UV diffuse reflectance spectroscopy was conducted on graphene oxide (GO), reduced graphene oxide (rGO), Co₃O₄, CoSnO₃, and rGO/CoSnO₃ nanocomposite. The results in Fig.7 indicate that pure Co₃O₄ nanoparticles displayed a

notable UV absorption edge at 800 nm. However, the UV absorption of other samples changed towards longer wavelengths. The variations in the absorption edges indicate alterations in the band structure. The bandgap of samples is obtained using the Kubelka-Munk function equation.



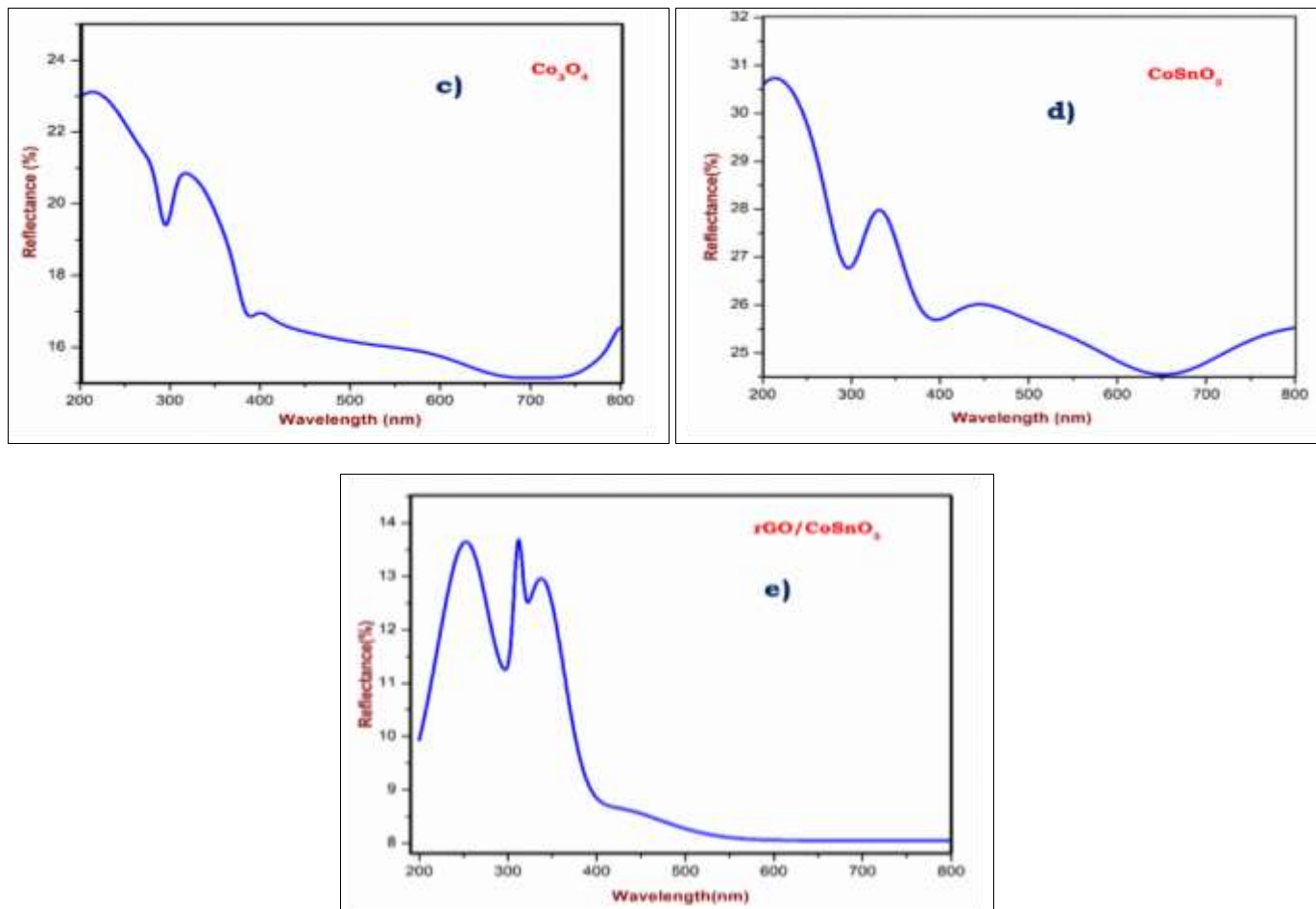
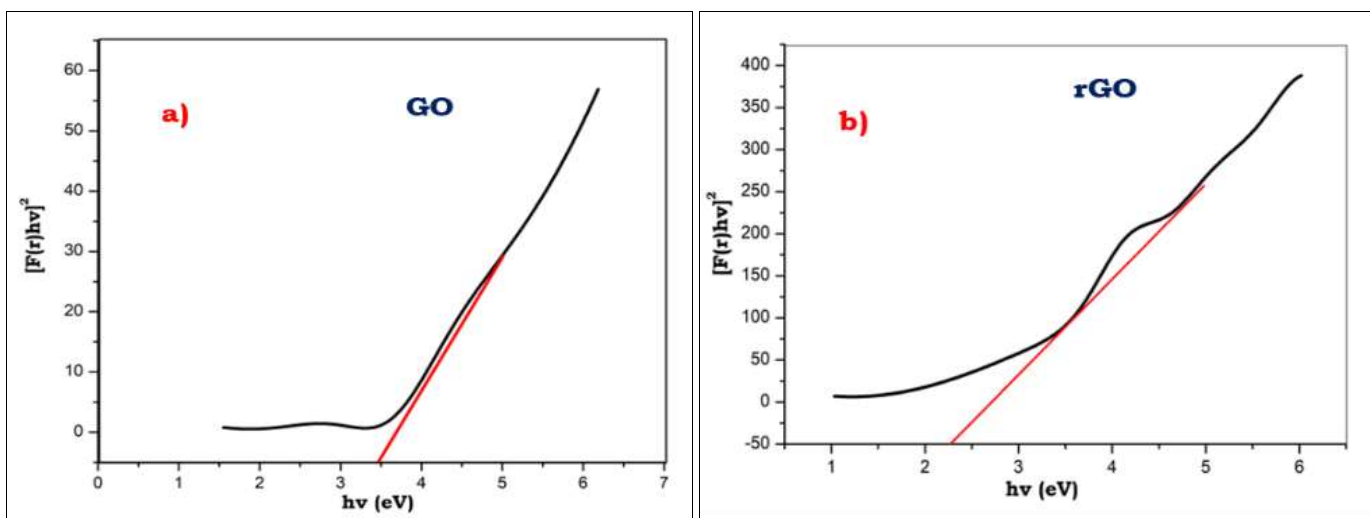


Fig 7: UV-DRS Image of (a) GO, (b) rGO, (c) Co₃O₄, (d) CoSnO₃ and (e) rGO/CoSnO₃

$$\alpha h\nu = A (h\nu - E_g)^n \tag{2}$$

α represents the absorption coefficient and $h\nu$ stands for the incident photon energy. The bandgap energies are derived from the intercept of the tangents, as illustrated in Figure 8. The band gaps of the produced materials are as follows: GO

(3.5 eV), rGO (2.4 eV), Co₃O₄ (4.5 eV), CoSnO₃ (2.7 eV), and rGO/ CoSnO₃ nanocomposite (1.6 eV). Oxygen vacancies can provide impurity levels close to the valence band, resulting in a reduced band gap value and higher catalytic activity in rGO/ CoSnO₃ compared to GO, rGO, Co₃O₄, and CoSnO₃ materials.



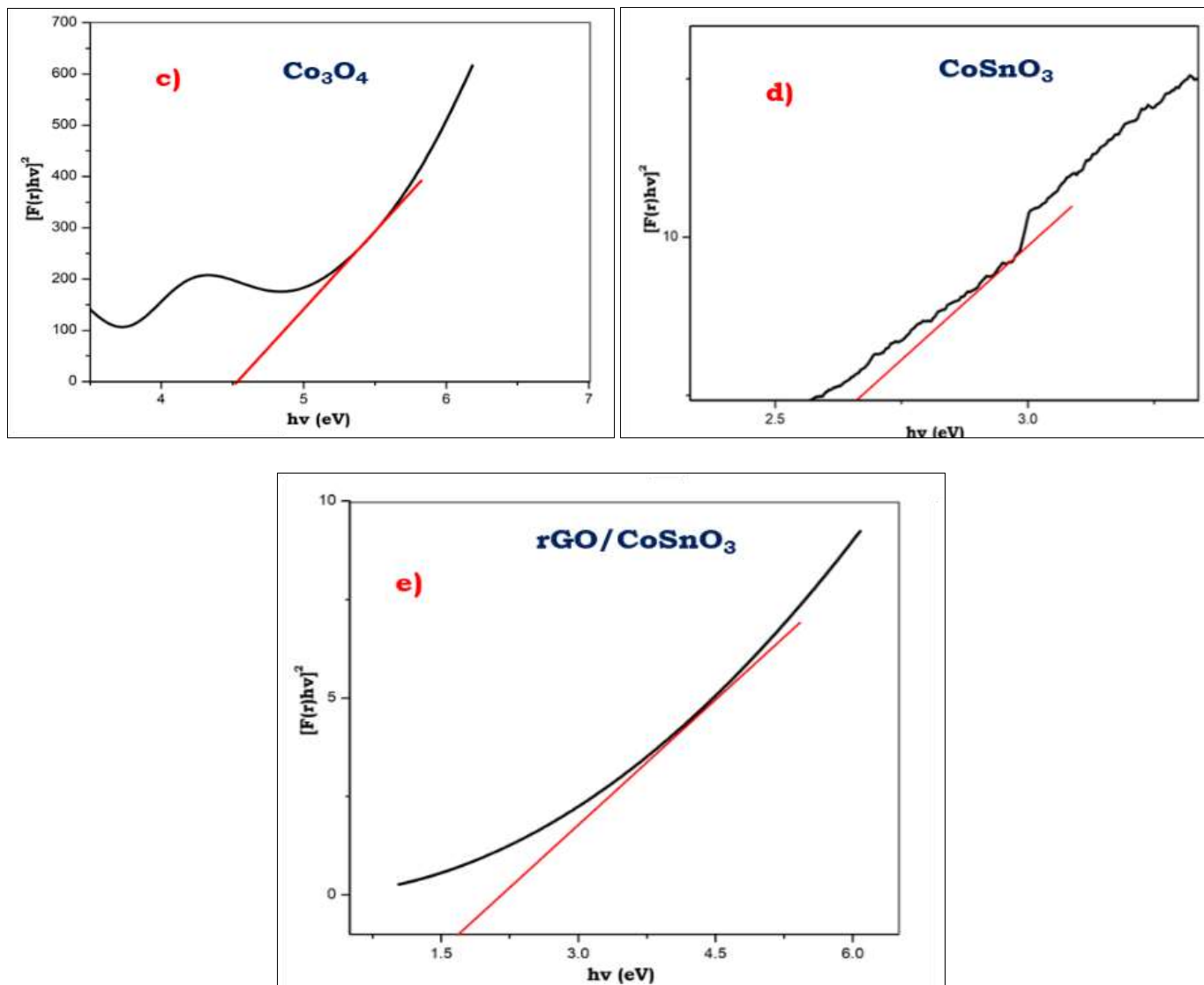


Fig 8: Tauc's Plot of (a) GO, (b) rGO, (c) Co_3O_4 , (d) CoSnO_3 and (e) rGO/CoSnO_3

Degradation percentages gradually increased with increasing the weight percentage of the catalyst and compared to the irradiation of sunlight and UV-light, sunlight irradiation is

most preferred and efficient process for the photocatalytic degradation process.

Table 2: Comparison of Degradation Percentage under Sun-light Irradiation

S. No	Weight of Catalyst	Sample	Dye	Irradiation	Percentage (%)
1	10mg	Co_3O_4	Methylene blue	Sunlight	75.2%
	10mg	CoSnO_3	Methylene blue	Sunlight	85.3%
	10mg	rGO/CoSnO_3	Methylene blue	Sunlight	88.2%
2	20mg	Co_3O_4	Methylene blue	Sunlight	77.2%
	20mg	CoSnO_3	Methylene blue	Sunlight	88.3%
	20mg	rGO/CoSnO_3	Methylene blue	Sunlight	92.0%
3	30mg	Co_3O_4	Methylene blue	Sunlight	83.6%
	30mg	CoSnO_3	Methylene blue	Sunlight	85.8%
	30mg	rGO/CoSnO_3	Methylene blue	Sunlight	96.2%

Table 3: Comparison of Degradation Percentage under UV-light Irradiation

S. No	Weight of Catalyst	Sample	Dye	Irradiation	Percentage (%)
1	10mg	Co_3O_4	Methylene blue	UV-light	40.0%
	10mg	CoSnO_3	Methylene blue	UV-light	44.4%
	10mg	rGO/CoSnO_3	Methylene blue	UV-light	48.0%
2	20mg	Co_3O_4	Methylene blue	UV-light	55.3%
	20mg	CoSnO_3	Methylene blue	UV-light	57.0%
	20mg	rGO/CoSnO_3	Methylene blue	UV-light	72.0%
3	30mg	Co_3O_4	Methylene blue	UV-light	62.0%
	30mg	CoSnO_3	Methylene blue	UV-light	72.0%
	30mg	rGO/CoSnO_3	Methylene blue	UV-light	75.2%

4. Conclusion

Nanomaterials such as GO, rGO, Co₃O₄, CoSnO₃, and rGO/CoSnO₃ were synthesized using the hydrothermal method. After calcination at 450 °C for 6 hours, cobalt oxide and cobalt tin oxide transformed into Co₃O₄ and CoSnO₃, resulting in the formation of rGO/CoSnO₃ nanomaterials. The nanomaterials exhibited crystalline sizes of 26.9 nm, 40.3nm, and 50.4 nm, and possessed cubic and agglomerated structures. The Kubelka-Munk function plot analyzed the band gaps of rGO, Co₃O₄, CoSnO₃, and rGO/CoSnO₃ as 3.0, 3.5, 2.4, 4.5, 2.7, and 1.6 eV, respectively. The photocatalytic efficiency of the prepared Co₃O₄, CoSnO₃, and rGO/CoSnO₃ in degrading methylene blue dye was assessed under sunshine and UV-light exposure using varying weight percentages of the catalyst. The rGO/CoSnO₃ nanocomposite exhibits superior degrading efficiency (96.2%) in comparison to bare materials such as Co₃O₄ (83.6%) and CoSnO₃ (85.8%). Sunlight is a more favorable source for eco-friendly photocatalytic degradation processes when compared to UV-light and sunlight irradiation. According to electrochemical studies, CoSnO₃ and rGO/CoSnO₃ electrodes have notable areal capacitance values of 158.8 F/g and 499.7 F/g at a scan rate of 10 mV/s, respectively. The rGO/CoSnO₃ electrode exhibited a higher specific capacitance of 603.12 F/g at 1 A/g compared to the CoSnO₃ electrode, which had a specific capacitance of 285.3 F/g at 1 A/g, as indicated by their charge-discharge curves. The rGO/CoSnO₃ electrode demonstrates a 95.7% cycle retention rate, even after 1000 cycles. The symmetrical electrode device demonstrated that rGO/CoSnO₃ has higher capacitance compared to pure CoSnO₃. Calculating the manufactured nano materials for usage as a capacitor in energy storage and for minimizing water pollution through efficient photodegradation processes.

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