The influence of irradiation time and layer thickness on the optical properties of NiO/CO_3O_4 nanocomposite for optoelectronic applications

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This paper offers insights into optical properties of NiO/Co_3O_4 nanocomposite, demonstrating how X-ray irradiation affects it which offers information for optoelectronic applications. FTIR results showed existence of chemical bonds that have been presented in our composite. The HRTEM images revealed the presence of clusters of molecules in various shapes and an average grain size approaching 19 nanometers. The optical investigations shows an increase in optical absorbance of a NiO/Co_3O_4 nanocomposite after irradiation with X-rays up to 60 min. The calculated indirect energy gap of the material increases response to X-ray radiation which attributed to defects in the material's crystal structure.

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Keywords: NiO/Co_3O_4, Structural, Optical properties, Nanosized, Medical applications

1. Introduction

Mixed nanometal oxides have various applications in nanotechnology, such as gas sensors, solar cells, batteries, catalysis, and optoelectronics. Some examples of mixed nanometal oxides are ZnO-TiO2, $CoFe_2O_4$@$BaTiO_3$, and Fe_3O_4@NiO[1] [2]. These nanomaterials can exhibit enhanced properties compared to their single metal oxide counterparts, such as higher surface area, improved stability, and tunable band gap [2]. Mixed nanometal oxides can be synthesized by various methods, such as sol-gel, hydrothermal, co-precipitation, and microwave-assisted techniques[2]. The synthesis parameters, such as temperature, pH, and precursor ratio, can affect the morphology, size, and composition of the mixed nanometal oxides[2]. NiO and Co_3O_4 are two metal oxides that can form a mixed nanometal oxide with various applications in catalysis, supercapacitors, and gas sensors. NiO/Co3O4 nanocomposites can be produced using a variety of techniques, including spray pyrolysis, sol-gel, and co-precipitation [3][4][5]. The Ni/Co mass ratio and the loading of NiO-Co_3O_4 can affect the morphology, size, composition, and performance of the nanocomposites[13]. It can exhibit high specific capacitance, excellent power density, and energy density as supercapacitor electrode materials[4]. They can also show high catalytic activity and selectivity for hydrogenation reactions[5] which are promising nanomaterials for energy and environmental applications[6]. These mixed nanometal oxides may find use in medicine as therapeutic agents, anticancer, antibacterial, antiviral, antifungal, and antileishmanial agents [7][8]. NiO/Co_3O_4 can prevent the formation of biofilms and quorum sensing, which are mechanisms of bacterial communication and resistance[8]. These nanoparticles can be used as therapeutic agents for diseases caused by oxidative stress, such as diabetes, Alzheimer's, and Parkinson's, by scavenging free radicals and reducing inflammation[7]. These nanoparticles can also induce apoptosis (cell death) in cancer cells and as drug delivery vehicles, by loading them with drugs such as doxorubicin and curcumin, and enhancing their solubility, stability, and targeting[7][9][10].

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In this study, NiO/Co_3O_4 nanoparticles were prepared. Various structural investigations have been done using XRD and HRTEM. The structural investigation examined how the introduction of NiO/Co_3O_4 can modified. Optical properties were extensively studied. Linear and mass attenuation coefficient were calculated as medical parameters. We believe that the findings from our research could be beneficial for several implications for various fields, including material science, nanotechnology, optoelectronics, and the development of new medical applications.

2. Experimental techniques

A flask with 25 mL of a 0.2 M $CO(NH_2)_2$ $6H_2O$ solution and 25 mL of a 0.2 M $Ni(NO_3)$ $2.6H_2O$ solution was used. After that, the flask containing the solution was put in the microwave and cooked for 20 minutes on full power. The detailed procedures were reported elsewhere [11][12]. The extraction of NiO NPs results in a black fine powder. The characterizations are done on the final products. $Co(NO_3)_3.9H_2O$ is used as a starting material for Co_3O_4 NPs, following the same procedure. Several widely used methods for producing mixed oxides such as sol gel, microwave-assisted combustion, and co-precipitation. One of two methods for combining two metal oxides, M1-O-M2 chemical bonding, or mechanical mixing with weak van der Waals forces, is what M1O and M2O represent. The metal nitrates is utilized to prepare the current mixed oxides. 0.5 $Co(NO_3)_3.9H_2O$ is used for $NiO/0.5Co_3O_4$ weight percent NPs. These NPs are made into films by dropping their water solution onto regular glass substrates that have been cleaned using ethanol, acetone, and distilled water. Next, a solvent drying is carried out on a hot plate for 10 minutes at 110 oC. The film is heated to 100 degrees Celsius for thirty minutes [13] [14][15].

A Shimadzu XD-3A with monochromatized CuKa radiation, λ=0.154 nm. X-ray diffraction (XRD) studies in 2θ of (30-80^o) were used. High transmission electron microscopy (HRTEM) images from the JEOL-JEM 200CX at 80 kV. At room temperature, the optical transmittance (T) and reflectance (R) were measured with a double-beam spectrophotometer.

3. Results and discussions

3.1. Structural investigations

A systematic study of the XRD was performed for NiO/Co_3O_4 nanocomposites. The details of XRD for NiO and Co_3O_4 NPs were examined in our previous works [15,16]. Substitutional alloys are composed of two metallic components with comparable atomic radii and chemical bonding characteristics. Solubility is further limited when two metals' radii are more than 15% different. For an interstitial alloy to form, a component present in the interstitial positions among the solvent atoms must have a covalent radius that is notably smaller than the solvent atoms. Nonmetals that form bonds with nearby atoms are typically interstitial elements [16]. Ni2+, the host material, has an ionic radius of 69 pm [17].

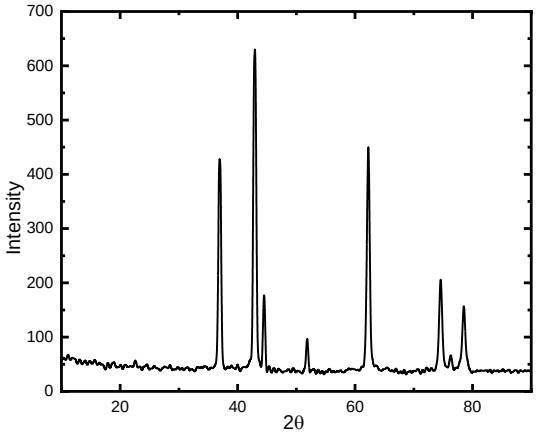

Fig. 1. XRD of NiO/Co_3O_4 nanocomposite [15,16].

As an additional material in the same coordination, the radius of Co^{2+} is 65 pm [18]. The formation of substitution alloys would be possible if the ionic radius of Co^{2+} were noticeably smaller than that of Ni^{2+}. The XRD chart of the NiO/Co_2O_3 nanocomposites are displayed in Figure 1. Eight distinct peaks can be seen in the NiO spectrum with 50 wt% of Co_3O_4 NPs, for more explanation see [15, 16].

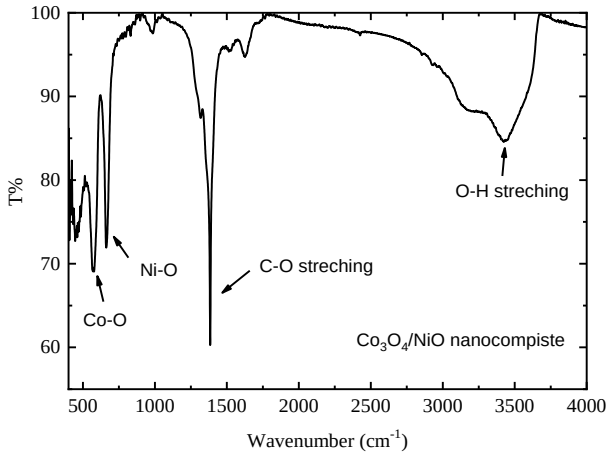

Fig. 2. FTIR of NiO/Co_3O_4 nanocomposite.

FTIR, is used in morphology investigation. FTIR is used to analyze functional groups of nanometal oxides. It provides information about chemical bonding and the composition of the materials. FTIR of Co_3O_4/NiO nanocomposite is shown in Figure 2. The FTIR assured the existence of the pair of nano-oxides with the sample. The peaks at 550 cm^{-1} and 650 cm^{-1} correspond to Co-O and Ni-O, respectively. There are broad peaks at 3450 cm^{-1} and 1380 cm^{-1} for O-H stretching vibrations and C-O stretching vibrations, respectively. These chemical bonds that have been presented in our novel composite can significantly influence its optical properties, especially in materials used in optoelectronics. Metal-oxygen bonds have a great effect on the absorption and reflection of light, as well as the material's bandgap energy, which is crucial for determining its optical properties which could be important for designing and optimizing materials for optoelectronics.

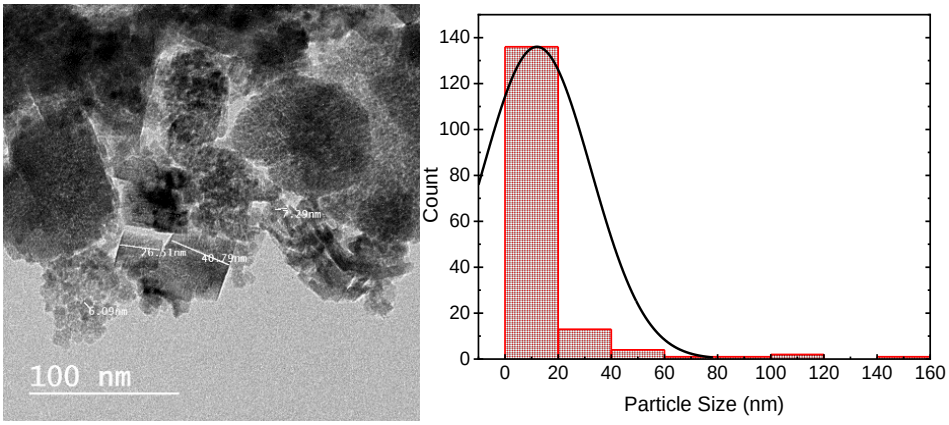

Fig. 3. HR-TEM images with two magnifications and particle size distribution NiO/Co_3O_4 nanocomposite.

HRTEM microscopy is used to characterize the morphology and crystal structure of the nanometal oxides at the atomic level. It provides high-resolution images that can reveal the size, shape, and crystallinity of the nanoparticles, as well as information about defects and lattice planes. HRTEM images of NiO/Co_3O_4 nanocomposite are shown in Figure 3a. As shown in Fig., the images revealed the presence of clusters of molecules in various shapes and an average grain size approaching 19 nm. This aggregation can affect the material's structural properties, such as the grain size distribution, surface area, and porosity. Aggregated grains can lead to increased light scattering within the material, altering its transparency. In addition, aggregation of grains influences quantum confinement effects and alters the material's optical bandgap and electronic transitions. Image J program shows the distribution of particle size which shows the average particle size in the range of 20 nm as shown in Figure 3b.

3.2. Optical investigations

Optical switching/limiting and absorption materials have drawn the attention of researchers due to the intricate nonlinear susceptibilities that complex optical phenomena in optoelectronic applications have to do with the interaction of intense laser beams with nanostructured material. Because of this, a variety of nanostructures have been employed to improve the optical properties [19]. Linear optical analysis aims to assess various optical parameters and constants and forecast their possible uses. Critical optical parameters for new composites, such as optical bandgap, localized state and skin depth can be computed using the estimated absorbance values.

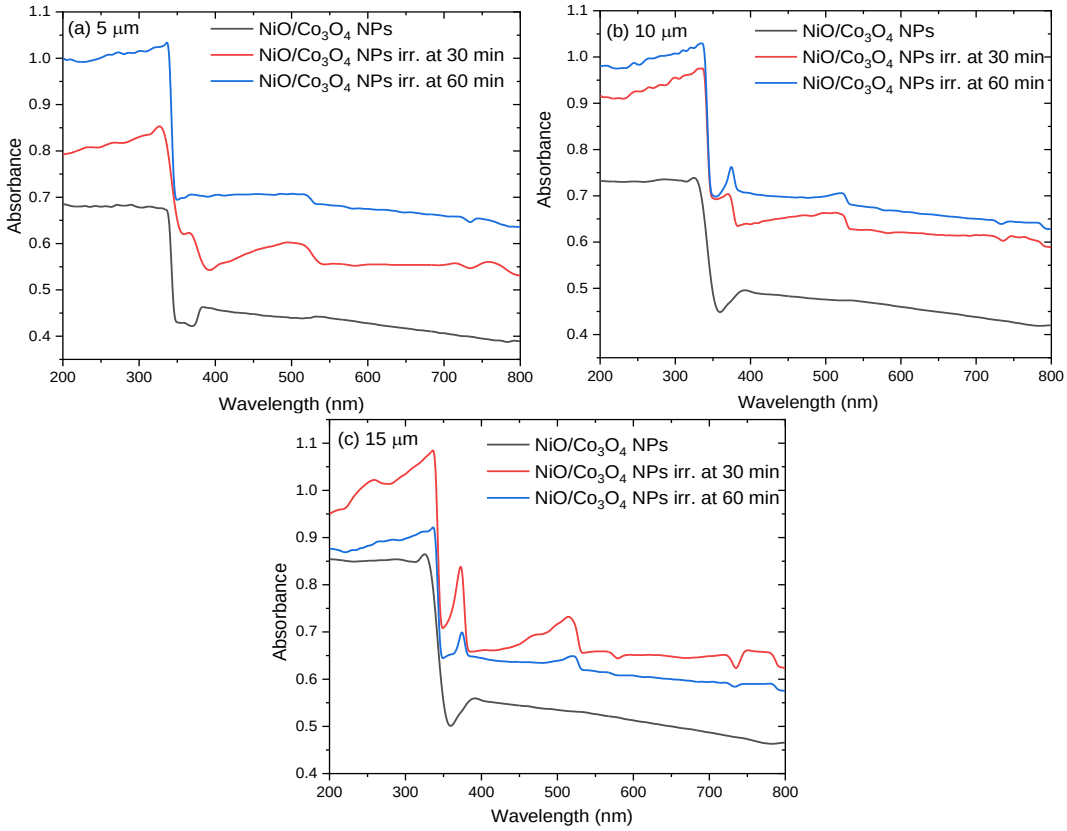

Fig. 4. Absorbance spectra of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

Figure 4a and Figure 4b show the effect of irradiation time on optical absorbance of NiO/Co_3O_4 nanocomposite films with a film thickness of 5, 10 and 15 µm, respectively. As noted, an increase in optical absorbance of NiO/Co_3O_4 nanocomposite after irradiation with X-rays up to

60 min. This could be due to the introduced defects in the crystal lattice of the nanocomposite, which can act as additional absorption centers for photons, leading to an increase in optical absorbance. Furthermore, the generation of e-h pairs in the material increases the density of charge carriers.

Figure 5 illustrates the effect of film thickness on absorbance spectra of NiO/Co_3O_4 nanocomposite with different irradiation XRD time. It is illustrated that absorbance increases as the film thickness increases. When wavelength (λ) decreases (photon energy increases), photons will be transmitted because they lack the energy to interact with atoms at high values of wavelength. The material will interact with the incident light, increasing the absorbance in the process[20].

The absorption coefficient, α, was calculated using the formula [21]:

$$\alpha = 2.303\frac{A}{d}, \; d\text{: thickness} \tag{1}$$

Figure 6 depicts the values of α on hν of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

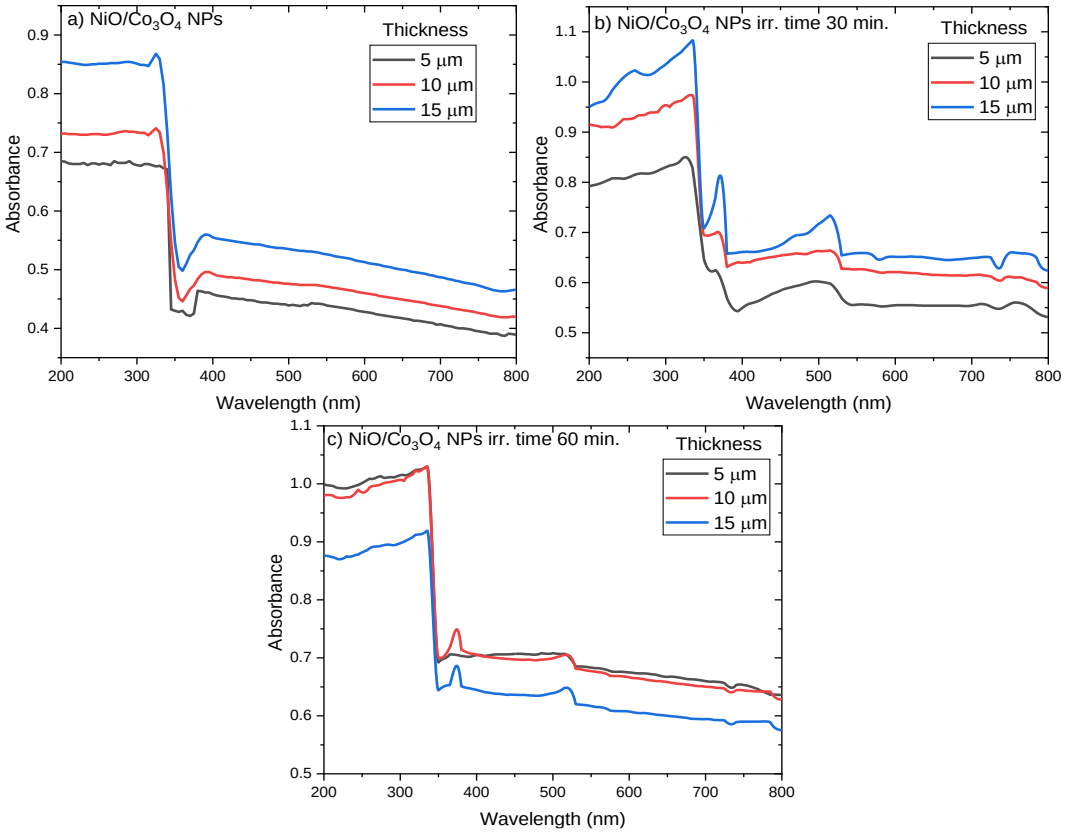

Fig. 5. Absorbance spectra of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

It is worth noting that, the absorption in the UV region was increased by 33 % and 26% for the sample thicknesses of 5 and 15 µm, respectively. This means the material with high thickness under investigation exhibits a decrease in light absorption in the UV region as a result of X-ray irradiation. The X-ray irradiation may cause a reduction in light absorption in the UV region due to alterations in the material's optical properties or the creation of new energy levels that influence its absorption behavior. The absorption intensity clearly exhibits an exponential decrease with wavelength. Such behavior is typical of many semiconductors and can be caused by a multitude of factors, including internal electric fields within the crystal, strain from imperfection-induced lattice deformation, and inelastic scattering of charge carriers by phonons. It is evident from the data that

there is a higher absorption of shifts. This change in absorption is explained by the nanocomposite's size reduction brought on by XRD irradiation [22].

Skin depth, δ calculations are important in various fields, including engineering and materials science, as they provide insights into the behavior of electromagnetic wave propagation in different materials. The skin depth can be calculated by[23]:

$$\delta = 1/\alpha \tag{2}$$

The δ on hν of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time is illustrated in Figure 7.

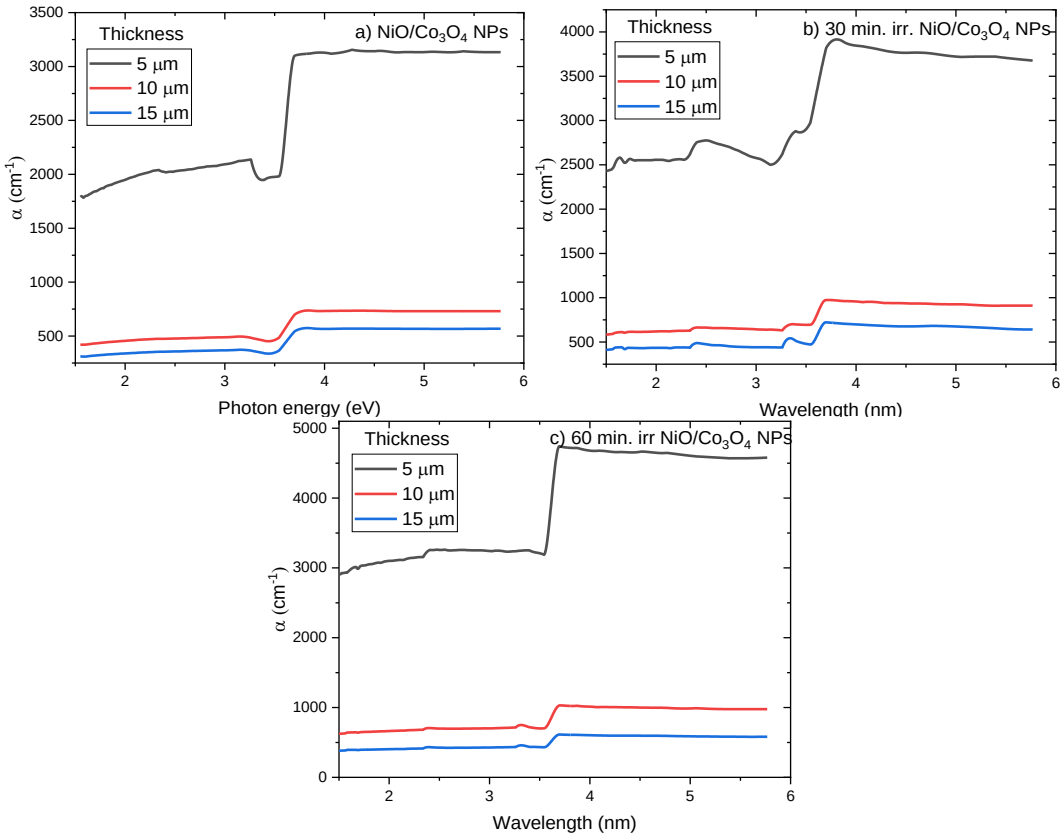

Fig. 6. Absorption coefficient (α) versus (hν) of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

As we can notified from the Figure 7, the skin depth increases as the thickness increases. This is because the increased thickness allows for greater penetration of electromagnetic waves into the material. The conductivity affects how quickly the wave's intensity decreases as it penetrates the material.

According to the WDD, Wemple-Dedmonico, model the optical energy gap, E_g, of NiO/Co_3O_4 nanocomposite by using [24][25]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g^{in}) \text{ for indirect transition} \tag{3}$$

$$(\alpha h\nu)^{2} = A(h\nu - E_g^{di}) \text{ for direct transition} \tag{4}$$

A: constant, E_g: optical band gap. Figures 8, 9 illustrated $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus hν of NiO/Co_3O_4 nanocomposite with different thickness at different irradiation XRD time.

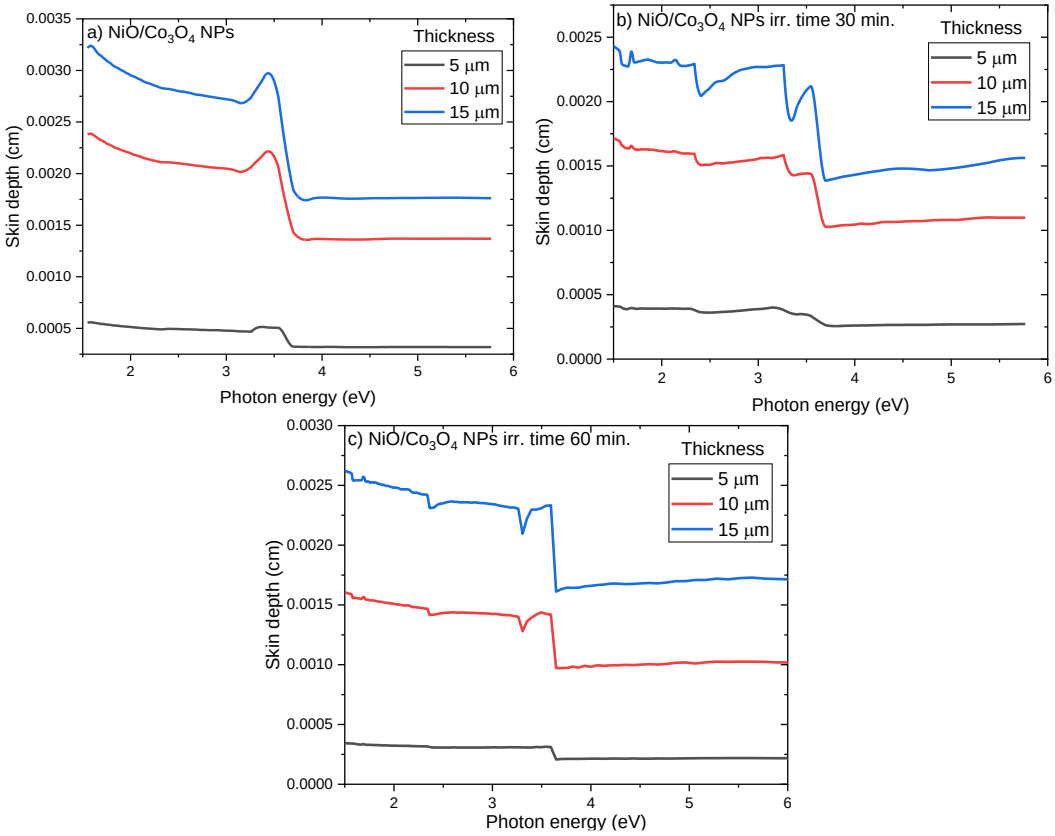

Fig. 7. Skin depth versus (hv) of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

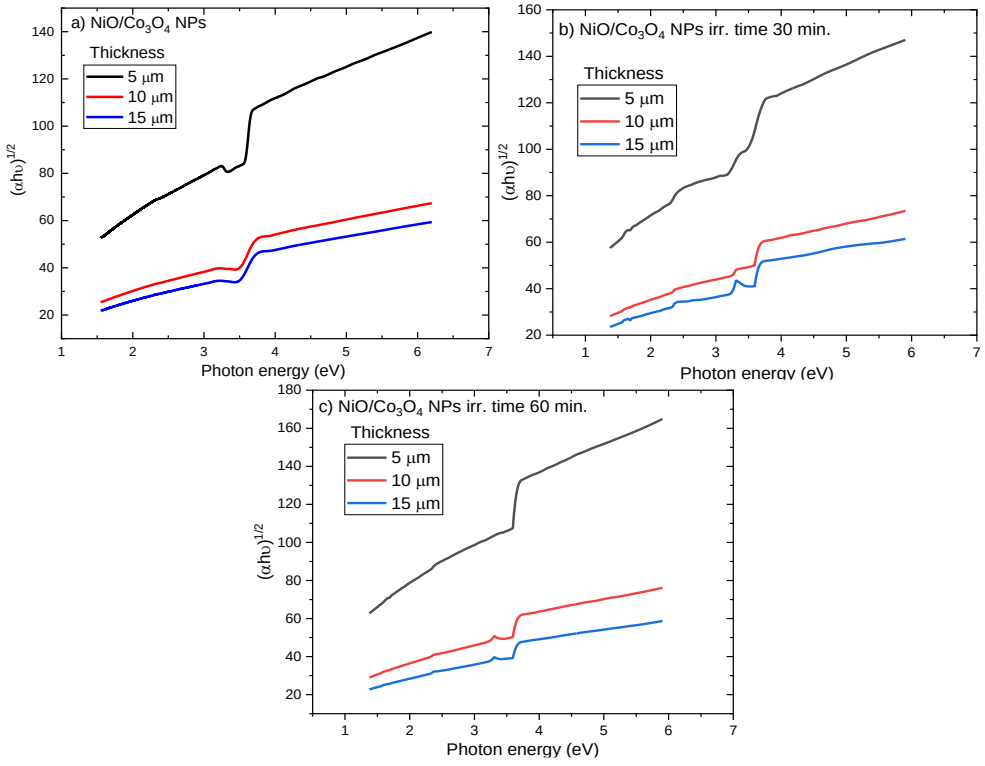

Fig. 8. $(\alpha hv)^{1/2}$ versus (hv) of NiO/Co_3O_4 nanocomposite with different film thickness at different irradiation XRD time.

The values of indirect and direct optical bad gap (E_g) of NiO/Co_3O_4 nanocomposite could be calculated by the extrapolating the tangent with the x-axis. All the calculated values have been listed in Table 1. Form these figures, the dominate transition is indirect transition, moreover, the table results illustrates the indirect energy gap of NiO/Co_3O_4 nanocomposite increases with increasing X-ray radiation time, while the direct energy gap almost remains constant. The increase in the indirect energy gap of the material in response to X-ray radiation could be related to the introduction of flaws or changes in the crystal structure of the substance.

X-ray irradiation can induce changes in the electronic states of the material by causing vacancy formation or modifying the local atomic arrangement. These changes can lead to a widening of the indirect energy gap, affecting the material's optical and electronic properties. The direct energy gap remains constant under X-ray radiation suggests that the changes induced by the radiation predominantly impact the material's indirect energy gap. The stability of the direct energy gap indicates that the fundamental electronic transitions responsible for the material's optical properties remain unchanged, despite the radiation exposure.

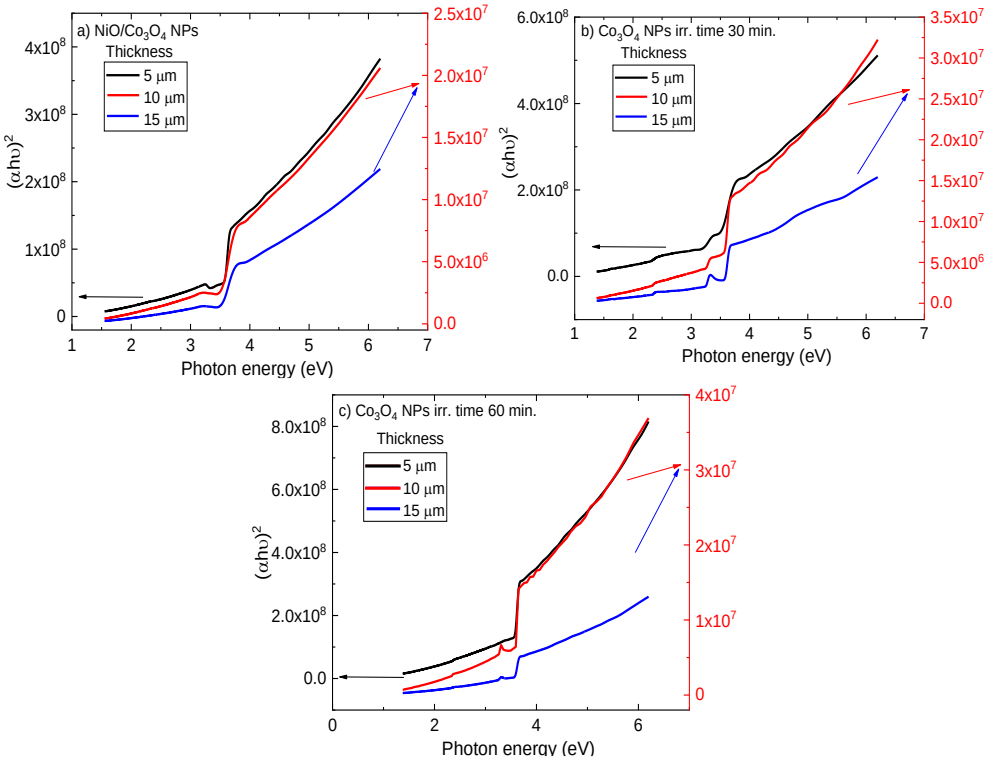

Fig. 9. $(\alpha hv)^2$ versus photon energy (hv) of NiO/Co_3O_4 nancomposite with different film thickness at different irradiation XRD time.

Table 1. Both values of direct and indirect optical band gap of theCo_3O_4-NiO nancomposite at different thickness with different XRD dose of irradiation time.

Thickness (μm)	**Irradiation time (min)**	***Eg* (indirect bad gap), eV**	***Eg* (direct bad gap), eV**
5	0	1.9	3.15
	30	2.9	3.3
	60	3.0	3.5
10	0	2.7	3.5
	30	2.9	3.4
	60	3.0	3.3
15	0	3.36	3.48
	30	3.50	3.50
	60	3.33	3.49

4. Conclusion

New findings regarding how X-ray irradiation affects the material's optical characteristics give valuable information for creating novel NiO/Co_3O_4 nanocomposite. The optical properties of the present composite can be greatly influenced by the presence of chemical bonds, as demonstrated by the FTIR results. This is particularly true for materials used in optoelectronics. The average grain size approached 19 nm. Moreover, HRTEM images showed the presence of clusters of molecules in a variety of shapes. An increase in optical absorbance of a NiO/Co_3O_4 nanocomposite has been observed by optical investigations following up to 60 minutes of X-ray irradiation. As a result of the introduction of defects or changes to the material's crystal structure, the calculated indirect energy gap of the material increases at different thicknesses in response to X-ray radiation which could help for optoelectronic applications.

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