Estimation of hydrothermally synthesized Iron incorporated 2D-sheet-like $\alpha$-MoO$_3$ microstructural and optical parameters treated by annealing temperature

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Abstract

In this article, pure and Fe-doped (5 wt.%) $\alpha$-MoO$_3$ nanosheets have been synthesized by hydrothermal approach and doped nanosheets were further annealed (at $T_a = 600$ °C and $T_a = 700$ °C temperatures for 3 hrs) for improved crystalline properties. The XRD analysis revealed the formation of orthorhombic structure without tracing of impurities or secondary phases. The iron dopant and annealing temperatures improved the crystallinity as the crystallite size increased. The pristine sample consists with randomly oriented nanosheets with an average width of 100–200 nm and length of several micrometers. Doping with iron does not induce any noticeable effect on morphology of $\alpha$-MoO$_3$, as revealed by FESEM imaging. The doped nanosheets form a large, rectangular plate-type layered structure at 600 °C. Nanosheets with more developed and smooth surfaces with sharp corners and edges were observed at an elevated temperature of 700 °C. EDX study confirmed the Fe incorporation. The presence of different functional groups was analyzed by FTIR spectra. As a result of Fe doping, the band gap has decreased by 10% from an intrinsic value of $\sim 3.00$ eV. The thermal annealing step further modifies the optical bandgap, providing an extracted value of 2.85 eV in this study.

1. Introduction

Dilute magnetic semiconductors (DMSs) are a special class of materials exhibiting both semiconductor and room temperature ferromagnetic properties at the same time. This simultaneous semiconducting and magnetic effects are obtained by controlled doping of suitable transition metal atoms with unpaired d electrons into diamagnetic semiconductor materials [1, 2]. The unique spin dependent magneto-electro-optical properties of DMSs are promising for wide range of potential applications in the emerging fields of novel logic, memory and optical devices as well as in transparent conductors, gas sensors, photo-catalytic and photovoltaic solar cells etc. [3]. These have led to a widespread interest and investigations of DMS materials within the condensed matter physics and materials science community over the last ten years. The non-magnetic host materials for DMSs are conventional semiconductors such as ZnO, SnO$_2$, TiO$_2$, MoO$_3$, In$_2$O$_3$ etc. Suitable transitions metal (TM) dopants are incorporated into cation sites of these hosts to produce DMSs, in which both charge and spin of the carriers can be simultaneously utilized [2, 4–8].

Among several candidates for non-magnetic host materials of DMS, molybdenum trioxide (MoO$_3$) is one of the most promising and heavily investigated multifunctional transitional metal oxides (TMOs). MoO$_3$ is an wide band gap II-VI semiconductor (intrinsic n-type) with a direct band gap in the range of 2.8–3.2 eV at room temperature.
It also exhibits rich chemistry associated with multiple valence states, high thermal–chemical stability, suitable electro-optical properties and hence, holds high potential for realizing novel logic, memory, optoelectronic and sensing devices [10]. MoO₃ is also promising for numerous technological applications in the fields of transparent conductors, photocatalysis, photovoltaics and organic light emitting diodes (OLEDs) etc [7, 11, 12]. There are three basic crystal structures of MoO₃. The well-known thermodynamically stable orthorhombic MoO₃ phase (α-MoO₃) has a MoO₆ octahedral base in its unit cell, where all of the MoO₃ components share edges and corners forming a zigzag chain and layered structure [13]. Two metastable phases which consist of the monoclinic MoO₃ phase (β-MoO₃) and hexagonal MoO₃ phase (h-MoO₃) [14].

Modification of physical properties of the MoO₃ nano-materials is necessary to widen its applications. For example, bandgap engineering or tuning of semiconducting materials is a very important method for modifying their electro-optical properties and implementing efficient semiconductor devices. Bandgap tuning can be performed by applying several different techniques such as doping, annealing, changing of fabricating methods etc [15–17]. Among various methods, doping is a simple and very effective way to alter and/or improve magneto-euro-optical properties of basis materials, which is obtained by a controlled incorporation of suitable extrinsic elements into specific sites of the host matrix [18, 19]. Thus, properties of MoO₃ can be changed by alloying it with suitable elements, for example, doping with niobium (Nb) [20], cerium (Ce) [19], tin (Sn) [21], gadolinium (Gd) [14], tungsten (W) [22], indium (In), cadmium (Cd) [23], nickel (Ni) [24], cobalt (Co) [7], dysprosium (Dy) [25], europium (Eu) [26], Silver (Ag) [27], Zinc (Zn) [28] etc have been reported in the literature for tuning various properties of MoO₃.

From literature survey, the hydrothermal technique offers most convenient and easy approach etc have been applied to improve the performance of undoped and doped nanostructured α-MoO₃ material [19, 36, 37]. From literature survey, the hydrothermal technique offers most convenient and easy method for improved crystalline properties. Finally, an efficient study is performed to divulge the influence of Fe-doping and annealing temperature on the microstructural (lattice parameters, average crystallite size, crystallinity etc), surface morphology, functional and optical characteristics of α-MoO₃ nanosheets by using various characterization techniques such as FESEM, XRD, EDX, FTIR, and UV–vis spectroscopy.

2. Experimental details

2.1. Materials

The pure and iron-doped orthorhombic molybdenum trioxide (α-MoO₃:Fe) nanosheets were prepared using hydrothermal approach. All the chemicals were analytical grade, used without further purification and procured from Sigma Aldrich Ltd, USA. The lists of the chemicals are as follows:
1. Ammonium heptamolybdate tetrahydrate (AHM) (NH₄)₆Mo₇O₂₄·4H₂O, precursor material
2. Concentrated nitric acid (73%HNO₃)
3. Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, precursor for dopant)
4. Ethanol and
5. Deionized water

2.2. Nanosheets preparation
In a typical procedure of pure α-MoO₃, 0.618 g of AHM was dissolved in 25 ml of distilled H₂O to obtain aqueous solution of ammonium heptamolybdate tetrahydrate (AHM). A magnetic stirrer was used to stir the aqueous solution dynamically for 1 h at the rate of 75 rpm at room temperature. At room temperature, 2.5 ml of 73% nitric acid was mixed drop-wise into this aqueous solution under magnetic stirring for 40 min, which turned the aqueous solution into very clear solution. Afterwards, the as- acquired clear solution was transferred in an auto clave and heated at 130 °C for 36 hrs with pressure 30 psi. The precipitates were formed and residue was carefully washed for several times with distilled H₂O and ethanol and dried at 85 °C for 4 hrs by using a vacuum oven. The as-obtained powder was annealed in an electric furnace at 450 °C temperature for 2 hrs to get the α-MoO₃ nanosheets. The similar process was carried out for 5 wt.% Fe-doped α-MoO₃ (α-MoO₃: Fe) nanosheets and at first, adding iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) as the source material of iron (III) with ammonium heptamolybdate tetrahydrate (AHM). Further, 5 wt.% Fe-doped α-MoO₃ or α-MoO₃: Fe nanosheets were annealed in an electric furnace at Tₐ = 600 °C and Tₐ = 700 °C temperatures for 3 hrs. We defined the pure α-MoO₃, 5 wt.% Fe-doped α-MoO₃, 5 wt.% Fe-doped α-MoO₃ annealing at Tₐ = 600 °C and 5 wt.% Fe-doped α-MoO₃ annealing at Tₐ = 700 °C as S1, S2, S3 and S4, respectively. The possible chemical reaction during the formation of α-MoO₃ is given below:

\[
(NH_4)_6Mo_7O_{24}·4H_2O(aq) + 6HNO_3 \overset{130 \degree C}{\longrightarrow} 7MoO_3(s) + 6NH_4NO_3(aq) + 7H_2O(l)
\]

2.3. Characterization techniques
The structural properties of the pure, α-MoO₃: Fe and annealed samples were explored using x-ray diffractometer (model: 3040-X Pert PRO) from 5 to 75 degree of 2θ values at a scanning speed of 1° min⁻¹ at room temperature. The voltage and current used in this experiment were 40 kV and 30 mA, respectively where the wavelength of CuKα, radiation is of 1.540 56 Å. Field emission scanning electron microscope (FESEM) (Model: JEOL JSM-7600F) was used to analyze the surface morphology and energy dispersive x-ray spectroscopy (EDS) was used to identify the elements presence in the materials. With the help of Fourier transform infrared spectroscopy (FTIR-ATR, Model: Perkin Elmer Spectrum Two) in the range of 4000–400 cm⁻¹, we investigated the orthorhombic phase stabilities and presence of different functional groups of all α-MoO₃ nanosheet samples. To determine the band gap, the value of reflectance of the nanosheets were acquired from a UV–vis-NIR diffuse reflectance spectrophotometer (Lambda 1050, PerkinElmer, USA) in the λ value ranges from 250 to 800 nm.

3. Results and discussion
3.1. Structural characterization
The crystallographic structures and phase formation were analyzed by x-ray diffraction (XRD) measurements. Figure 1 exhibits the x-ray diffraction spectrum of synthesized pure (S1), doped (S2) and annealed (S3 and S4) α-MoO₃ samples. It is observed that the XRD peaks of representative sample are in well accordance with the orthorhombic phase of molybdenum trioxide according to the data card (JCPDS) No. 05–0508 (space group. Pbmm, a = 3.962 Å, b = 13.858 Å, c = 3.697 Å) [38–40]. Therefore, no peak of secondary phases can be detected thereby excluding the presence of any impurities and confirming the formation of high purities and single phase of all samples. The sharp and strong patterns indicate the well crystalline form of the nanomaterials. The identified diffraction peaks such as (020), (110), (040), (021), (060) and (081) are evidently separable and indicates the poly-crystalline nature. For pure α-MoO₃ sample, the higher intensities of diffraction peaks (0k0) [where k = 2, 4, 6] specify the evidence of highly anisotropic growth of the nanosheets [25, 41, 42]. The peak (040) at 25.8236° with maximum intensity of pure α-MoO₃ nanosheet refers preferred orientation and gradually shifted towards a lower diffraction angle after iron incorporation (2θ = 25.6494°) and annealing of as-deposited doped sample (2θ = 25.6435° for Tₐ = 600 °C, 2θ = 25.6412° for Tₐ = 700 °C), revealing the changes in inter-planar distance (d₀40). The estimated d₀40 values are shown in table 1, from which it is clearly
observed that the inter-planar distance increases after Fe-doping and also with increase of annealing temperatures. This result implies the existence of lattice strain in the crystal structures of α-MoO$_3$ nanosheets.

It is well recognized that the peak intensity measures the crystallinity whereas the FWHM related to the crystallite size of the samples. The sharp and narrow XRD peak suggests the larger crystallite size which inevitably improves the crystallinity of the products. For preferred diffracted peak (040), the peak intensity gradually increases and FWHM decreases from samples S1 to S4 as presented in figure 2 and table 1, which is due to the Fe-doping in the MoO$_3$ matrix and also raise the level of annealing temperature. This result reflects the gradual improvement of crystallinity of the nanosheets.

The x-ray diffraction pattern gives the information to reveal micro-structural details and different structural parameters. The lattice parameters ‘a’, ‘b’ and ‘c’ for orthorhombic molybdenum trioxide (α-MoO$_3$) of corresponding plane were determined using the formula [44]

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}. \quad (1)$$

Here, d denotes the inter-planar distance and the values of d can be calculated by using Bragg equation [7]

$$2d \sin \theta = n\lambda. \quad (2)$$

Here, n stands for the order of diffraction and the typical value is 1. The crystallite size (D) of nanosheets have been estimated from FWHM value of the most strong peak (040) by Debye–Scherrer’s relation [45]

$$D = \frac{K\lambda}{\beta \cos \theta}. \quad (3)$$

In this equation, $D$ denotes the crystallite size (in nm), $\theta$ is glancing angle (in degrees), $\lambda$ is the wavelength of CuK$_{\alpha}$ radiation ($\lambda = 1.54056$ Å), $K$ is a constant also known as shape factor ($K$ equals to 0.90) and $\beta$ is the full width at half maximum (FWHM) of the corresponding peak (in radians). The induced strain ($\varepsilon$) has been determined by the Stokes–Wilson formula [46] as

$$\varepsilon = \frac{\beta}{4 \tan \theta}. \quad (4)$$

The dislocation density ($\delta$) has been obtained from the following equation [47]

$$\delta = \frac{1}{D^2}. \quad (5)$$

The stacking fault (SF) is defined as the planar defect in the diffracted plane and estimated for corresponding plane (040) by the formula [48] as
Table 1. Variation of different structural parameters of pure (S1), Fe-doped (S2), annealed (S3 and S4) α-MoO₃ nanosheets.

| Samples | Position, 2θ (°) | FWHM (radians) | d-spacing (Å) | Crystallite size, D (nm) | Dislocation density, δ × 10¹⁴ (lines/m²) | Strain, ε (× 10⁻³) | Stacking fault, SF (× 10⁻⁴) | Lattice constants (Å) |
|---------|-----------------|----------------|---------------|--------------------------|----------------------------------------|-----------------|-------------------------|---------------------|
| S1      | 25.8236         | 0.3235         | 3.4478        | 25.19                    | 15.7544                                | 6.1581          | 29.87                   | 3.977 13.905 3.696   |
| S2      | 25.6494         | 0.3137         | 3.4703        | 25.97                    | 14.8244                                | 6.0127          | 29.06                   | 3.976 13.902 3.692   |
| S3      | 25.6435         | 0.1184         | 3.4711        | 68.81                    | 2.1119                                 | 2.2699          | 10.97                   | 3.970 13.880 3.690   |
| S4      | 25.6412         | 0.1148         | 3.4714        | 70.97                    | 1.9854                                 | 2.2011          | 10.64                   | 3.966 13.875 3.685   |
The values of different structural parameters estimated using the above-mentioned formulae are tabulated in table 1. The as-synthesized pure nanosheet are found to be $a = 3.977\, \text{Å}$, $b = 13.905\, \text{Å}$, $c = 3.696\, \text{Å}$. These determined values of lattice constants are very close to reported values [49]. The estimated crystallite sizes of preferred orientation $(040)$ are found to be 25.19 nm and 25.97 nm for the pure nanosheet (sample S1) and Fe-doped nanosheet (sample S2), respectively, whereas, the crystallite size increases from 68.81 to 70.97 nm after increasing annealing temperature from $600^\circ\text{C}$ (sample S3) to $700^\circ\text{C}$ (sample S4) of $\alpha$-MoO$_3$: Fe nanosheets. However, the crystallite size varies in the ranges from 25.19 to 70.97 nm from sample S1 to S4, which designates the existence of nano crystallites in the $\alpha$-MoO$_3$ nanosheet synthesized in this experiment. The enhance in crystallite size with Fe-doping and increase of annealing temperature shows the enhanced crystallinity which is due to the reducing of grain boundary discontinuities by larger crystals that reduces the total energy of the system [13, 49, 50]. The increase in crystallite size is related to decrease in strain and dislocation density. The value of strain and dislocation density declines after Fe incorporation and with increase of annealing temperatures that also reveals the enhancement of crystalline nature. And the stacking fault values also decrease from sample S1 to S4. As a consequence, the crystallinity and growth of the $\alpha$-MoO$_3$ nanosheet badly depends on the Fe-doping and annealing temperature.

![Figure 2](image.png)

**Figure 2.** Peak position and shifting of preferential orientation $(040)$ of pure (S1), Fe-doped (S2), annealed (S3 and S4) $\alpha$-MoO$_3$ nanosheets.

$$SF = \left[ \frac{2\pi^2}{45(3\, \tan \theta)^{3/2}} \right] \beta.$$  \hspace{1cm} (6)

### 3.2. Surface morphology

The representative morphologies and microstructures of the pure (S1), 5 wt.% Fe-doped $\alpha$-MoO$_3$ (S2) and annealed (S3 and S4) samples are characterized by FESEM observations as presented in figures 3(a)–(d) with (×30 000) magnification. From the overall morphology of pure $\alpha$-MoO$_3$ (figure 3(a)) it is observed that the product consists almost entirely of densely packed, smooth surfaces, perfectly straight and randomly oriented nanosheets with an average width of 100–200 nm and few microns long. The doped nanosheet (S2) has similar morphology with slight developed width and length as depicted in figure 3(b).

Annealing at $600^\circ\text{C}$ (S3), the 5 wt.% Fe-doped $\alpha$-MoO$_3$ nanosheets developed and converted to form a 2D large rectangular plate-type layered structure with an average width of about 2 micrometers and thickness of about 200 nm as presented in figure 3(c). The layered structures have smooth surfaces and sharp corners at their ends. At $700^\circ\text{C}$, the more developed layered structure was observed compare to sample S3 (annealed at $600^\circ\text{C}$) (figure 3(d)). Thus, it is observed that the enhancing the annealing temperature, the enhanced the growth rate with the variation of surface morphology of nanosheets is mainly due to the realization of different surface energy leading to nanocrystallites of varying nanocrystalline nature and size. As a consequence, it is simply decided that the doping and annealing temperature significantly effect the growth of the nanosheets.
3.3. Elemental analysis

As a small amount of Fe incorporation has a strong effect on physical properties e.g., structural and optical properties, so it is important to identify the elements presence in the products. Here, we used EDX spectrum to verify the presence of Fe (iron) doped in the \( \alpha \)-MoO\(_3\) nanosheets. Figure 4 shows the EDX spectrum of Fe-doped \( \alpha \)-MoO\(_3\) nanosheets. The EDX spectrum shows that the synthesized Fe-doped \( \alpha \)-MoO\(_3\) nanosheets are certainly composed of molybdenum (Mo), iron (Fe) and oxygen (O). The peak in the spectrum at 6.40 keV designates iron (Fe) element, while, two peaks at 0.525 and 2.293 keV confirm the existence of oxygen (O) and molybdenum (Mo), respectively.

3.4. Functional properties

The FTIR spectra in the values of wavenumber from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) (as our area of attention is from 1000 to 450 cm\(^{-1}\), it is limited the range up to 1100 cm\(^{-1}\)) as shown in figure 5, which confirmed the orthorhombic phase stabilities and presence of different functional groups of S1, S2, S3 and S4 nanosheets.

There are two major vibrational zones (i.e., 1000–600 and 600–400 cm\(^{-1}\)) were observed for all of pure, Fe-doped and annealed \( \alpha \)-MoO\(_3\) nanosheet samples. Each nanosheet sample showed four strong vibrational peaks. The IR spectra of pure \( \alpha \)-MoO\(_3\) nanosheet shows four strong vibrational peaks positioned at the wavenumber values of 539.97, 817.69, 85.41 and 992.08 cm\(^{-1}\), respectively, and a weak bond at 486.26 cm\(^{-1}\). This FTIR spectrum is well accordance with the layered orthorhombic crystallography of molybdenum trioxide [51]. The strong band at 992.08 cm\(^{-1}\), is related to the Mo = O stretching vibration, demonstrating the layered orthorhombic MoO\(_3\) structure [52–54] and this band is found at 992.78 cm\(^{-1}\), 989.23 cm\(^{-1}\) and 990.03 cm\(^{-1}\) for Fe-doped \( \alpha \)-MoO\(_3\), Fe-doped \( \alpha \)-MoO\(_3\) annealed at 600 °C, Fe-doped \( \alpha \)-MoO\(_3\) annealed at 700 °C, respectively.

The strong signal at 857.41 cm\(^{-1}\) is related to the Mo–O–Mo stretching vibration in \( \alpha \)-MoO\(_3\) nanosheet [55] and noticed at 843.21 cm\(^{-1}\) for Fe-doped sample. The Mo–O–Mo units gradually disappeared from sample S1 to S4. Another strong vibrational peak is found at 817.69 cm\(^{-1}\), 816.83 cm\(^{-1}\), 807.77 cm\(^{-1}\) and 812.40 cm\(^{-1}\) for sample S1, S2, S3 and S4, respectively. The peak at 539.97 cm\(^{-1}\) is associated with the bending vibrations of oxygen atom (O\(_{\text{3Mo}}\)) connected to 3Mo atoms ν(O–3Mo) in pure nanosheet [51, 54] and this bending vibration can be observed at 543.86 cm\(^{-1}\) for sample S2, although vibrational peak did not appear for annealed products.
A frail bond at 486.26 cm$^{-1}$ is ascribed to the Mo (2)–O (4) vibration with the H$_2$O molecule and the intensity reduced as enhancing of temperature from 600 to 700 °C which may be due to the effect of heat generation [56]. No water was detected in any nanosheet sample. It is clearly observed from FTIR spectra that all samples exhibit orthorhombic phase with the variations in band intensities and wavenumber values in different functional groups confirmed the successful incorporation of Fe ions in MoO$_3$ lattice structure and stability of orthorhombic crystal structure after annealing the sample.

### 3.5. Optical properties and band gap tuning

The optical absorption characterization of pure, Fe-doped α-MoO$_3$ and annealed nanosheet was performed by diffuse reflectance spectra (DRS) as depicted in figure 6. The samples exhibit reflectance peaks with gradual declined values at visible region with the incorporation of Fe and increasing annealing temperature. The sharp characteristic absorption band edge is found to be around 375 to 425 nm for each sheet and energy gap transition is attributed from it by absorbing light of visible range. The electronic band gap transition is attributed by the
absorption of visible light from the top of the valence band (which is mainly composed of O 2p orbital hybridized with Mo 4d) to the bottom of the conduction band (which is mainly composed of Mo 4d orbital hybridized with O 2p) [57].

The band gap energy, $E_g$ (eV) measurements were performed from absorption readings using the Kubelka-Munk (K-M) method as shown in figure 7. The Kubelka–Munk function is related to the diffuse reflectance as follows [54],

$$F(R) = (1 - R)^n / 2R.$$  \hspace{1cm} (7)

Further, $F(R)$ is proportional to absorption co-efficient ($\alpha$) as,

$$F(R) \propto \alpha = (\hbar \nu - E_g)^n / \hbar \nu.$$  \hspace{1cm} (8)
where, $F(R)$, $R$, $h\nu$ and $E_g$ (eV) denote the K-M function, diffuse reflectance value, incident photon energy, and band gap energy, respectively. It is observed the sharp linear region of the curve that indicates the direct bandgap type behavior of the samples. The power factor of the characteristic optical transition process ($n$) is equal to half in case of direct allowed transition of nanostructured $\alpha$-MoO$_3$. An extrapolation of the rectilinear part of the graph of $[F(R) \times h\nu]^2$ versus $h\nu$ to the $x$-axis and the intersection of the tangent line with $[F(R) \times h\nu]^2 = 0$ represents the value of $E_g$ of corresponding material. The values of $E_g$ are noticed to be 3.00 and 2.70 eV for pure and 5 wt.% Fe-doped $\alpha$-MoO$_3$ nanosheets, respectively. It is clear that the $E_g$ value after doping is less than that before incorporation of iron (Fe). This significant shifting of optical band gap energy to the visible range proves that the optical properties are obviously changed after iron (Fe) incorporation compared to pure $\alpha$-MoO$_3$ nanosheets. Iron act as a donor atom and some Mo$^{6+}$ ions in MoO$_3$ matrix are replaced with transition metal ions (Fe$^{3+}$) that creates more energy levels in energy band. Furthermore, this may come from the influences of reduction of crystal defects, structural disorders and vacancies (oxygen vacancies) due to insertion of transition metal ions that supports the XRD results. In that case, one or more electrons are captured by vacancies and creates donor centers. Similar results for the reduction of optical bandgap after the incorporation of transition metal Fe$^{3+}$ ions in the ZnO, TiO$_2$, MnO$_2$ etc were reported by several research groups [58–60]. As a result, they build up the impurity band inward the forbidden gap region. These centers are in the forbidden gap and form a narrow donor band at about 0.30 eV below the conduction band. The red shifting in the band gap highlights the potential of the $\alpha$-MoO$_3$: Fe nanosheets not only as a promising photocatalyst but also low band gap optoelectronic and photonic device applications.

The annealing temperature has also noteworthy effects on the optical band gap of doped products. The estimated band gaps of annealed samples are 2.80 and 2.85 eV for S3 and S4, respectively. This blue shift in band gap can be assigned to the influence of lower value of defect concentration after increasing annealing temperature which consequently decreases the width of impurity states, and hereafter broadening the energy gap [61]. Jittiarporn et al reported the relation between defect concentration (oxygen vacancy) and broadening of optical bandgap as a function of substrate temperature [13]. Recently, Simichi et al observed the annealing temperature (400–500 °C) on the properties of MoO$_3$ and identified the orthorhombic structure [62]. They described that the value of optical bandgap increased due to suppression of the oxygen deficiency and formation of close to stoichiometric phases as annealing temperature increased. On the other hand, annealing temperature at (600–700 °C), the hopping-electron procedure between two dissimilar oxidation positions ($e^-$ shifting from Mo$^{5+}$ → Mo$^{6+}$) contributes to electrical conduction process by reducing the defect concentration, thereby increase in the optical band gap [43]. Therefore, annealing temperature is able of tuning the optical bandgap of $\alpha$-MoO$_3$: Fe nanosheets by modifying the structural parameters.

4. Conclusions

In this experiment, we have synthesized pure and 5wt.% Fe-doped $\alpha$-MoO$_3$ nanosheets through a facile hydrothermal route and the $\alpha$-MoO$_3$: Fe nanosheets were annealed in an electric furnace at $T_a = 600$ °C and $T_C = 700$ °C temperatures for 3 hrs. The XRD patterns show the pure sample is single orthorhombic phase and indicates the phase stability after Fe incorporation and annealing, supported by FTIR spectra. The EDX spectrum proves the incorporation of Fe in the $\alpha$-MoO$_3$ nanosheets. Characterizations displayed that Fe atoms replaced the Mo atoms into the crystals of MoO$_3$ without perishing or affecting the basic single crystal structure. After Fe incorporation, the overall morphology of $\alpha$-MoO$_3$ nanosheets has almost remain unaffected, explored by FESEM images. At 600 °C, the doped nanosheets developed and converted to form a 2D large rectangular plate-type layered structure whereas nanosheets with more developed and smooth surfaces with sharp corners and edges were observed at 700 °C. The doping and annealing temperatures improved the crystallinity as the crystallite size increased. The Fe incorporation reduces the optical bandgap of MoO$_3$ from 3.00 to 2.70 eV that is due to the induced defects, disorders and variation of micro strain. The noteworthy influence of annealing temperature on doped sample is also observed which increases the energy gap in the range of 2.70 to 2.85 eV. The enhancement of crystallinity and surface morphology, orthorhombic phase stability and improved optical properties clearly explored that our results have numerous significant scientific implementations in the fields of spintronic, optoelectronic and photonic devices.

Conflict of interest

There is no conflict of interests present.
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