Herein we report the first in situ hydrothermal-assisted synthesis of a MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite. The composite was prepared with various amounts of rGO loaded (1%, 3%, 5%, 7% and 10%), which were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy, scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectrophotometer, transmission electron microscopy, UV-visible diffuse reflectance spectrophotometer, thermogravimetric analysis (TGA), Raman, Photoluminescence and Brunauer–Emmett–Teller analysis to study the structural, morphological and optical properties. FESEM micrographs reveal a regularly uniform belt-type structure in which MoO$_3$ with relatively smooth surfaces and Fe$_2$O$_3$ were agglomerated, which led to complete dispersion with the rGO and formed ternary nanocomposites, MoO$_3$/Fe$_2$O$_3$/rGO. The elemental composition of the ternary nanocomposite (Mo, Fe, O and C) was determined from EDX. XRD results show the average crystallite size to be 22.3 nm for the ternary nanocomposite and about the same for the pure phase formation. The synthesized samples were examined for degradation of a model dye, methylene blue (MB) under visible light illumination. The photocatalytic degradation efficiency of as-synthesized materials was determined by measuring the absorption spectra of MB, and the results showed that MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite exhibited higher MB photodegradation efficiency (99.47%) under visible light illumination than other four rGO-loaded ternary nanocomposites, MoO$_3$/Fe$_2$O$_3$ binary composite, Fe$_2$O$_3$ and MoO$_3$.

1. Introduction

Scarcity of water has become a severe problem in recent years due to industrialization and urbanization. Many industries produce synthetic organic compounds, which are extremely hazardous due to their carcinogenic nature, for use in dyeing, printing, textiles, photography, cosmetics and foods their production leads to water contamination [1]. Organic
dyes are discharged into the environment in various ways, which research has shown to exert adverse effects on nearly 10–15% of the population as well as on aquatic life [2]. Industrial effluents must therefore be degraded or removed from contaminated water. There are several approaches to treating industrial effluents, including aerobic oxidation, reverse osmosis, ultra filtration, biosorption, chlorination, membrane filtration, liquid–liquid extraction adsorption, ion-exchange, advanced oxidation processes and heterogeneous photocatalysis [3,4]. In recent years, heterogeneous photocatalysis has received considerable attention for environmental applications [5]. Photocatalysis with solar energy and semiconductors is of a great importance for solving global energy and environmental issues [6]. It has been extensively used for air purification and wastewater treatment. Many semiconductors such as TiO$_2$, NiO, ZnO, MoO$_3$, ZrO$_2$, WO$_3$ and CdS have been reported as photocatalysts [7–12]. Among these metal oxides, molybdenum trioxide (MoO$_3$) is a well-known n-type semiconductor with a wide bandgap of 2.5–3.2 eV. Although molybdenum has oxidation states ranging from +2 to +6, molybdenum oxides exist mainly in two forms, Mo (IV) and Mo (VI) oxide [13]. In general, Mo (VI) oxide appears in one of three forms, orthorhombic (α-MoO$_3$), monoclinic (β-MoO$_3$) and hexagonal (h-MoO$_3$) [14,15]. The meta-stable β-MoO$_3$ and h-MoO$_3$ have been investigated intensively compared with thermodynamically stable α-MoO$_3$ due to their excellent physicochemical properties [16]. They show great potential for applications in electrochromic and photochromic devices, sensors, catalysts, lubricants, display materials, organic solar cells and cathode electrodes for lithium batteries [17–19].

Applications for three wide bandgap semiconductor materials are limited, because their relatively wide bandgaps can be excited only by UV light and rapid recombinations of photogenerated electron-hole pairs [20]. Many previous reports have shown that the charge separation efficiency of Fe$_2$O$_3$ can be increased by coupling with semiconductors, which suggests an unusual electron transfer from the CB of Fe$_2$O$_3$ to the CB of semiconductors.

But these binary composites always suffer a serious decrease in photocatalytic efficiency after several uses [21], possibly due to the chemical instability of Fe$_2$O$_3$ induced by photogenerated electrons transferred from various metal oxides [22]. In order to overcome this issue, hybridized Fe$_2$O$_3$ containing a binary nanocomposite with suitable support can be used to improve the photocatalytic activity. Graphene and graphene oxide (GO) are additional excellent new entrants into the photocatalysis field, which can support the nanocomposite in attaining effective degradation as it scavenges and shuttles electrons due to its electrical [23], mechanical [24] and thermal properties [25]; thus, the recombination issue can be diminished significantly. GO has a two-dimensional structure with a monolayer of sp$^2$ carbon atoms packed into a honeycomb crystal plane with unique mechanical and electrical properties. It offers a good opportunity to prepare composite materials for photocatalysis applications [26–29]. Researchers recently have shown their more interest in the preparation of rGO-based ternary composites, however such as Fe$_2$O$_3$–graphene–TiO$_2$ [30], Ag–ZnO/rGO, Ag–Ag–Br/TiO$_2$/rGO [31,32], Ag/TiO$_2$/rGO [33], CdS–Graphene–TiO$_2$ [34], Cu–P25 graphene ternary composite [35], Pt/titania/reduced graphite oxide [36], RGO/ZnS–Ag$_2$S [37], reduced graphene oxide/g-C$_3$N$_4$/Ag–AgCl [38], reduced graphene-oxide/TiO$_2$/ZnO [39], Au@r-GO/TiO$_2$ hybrids [40] and brilliant Blue/RGO/quaternary phosphonium salt composite [41]. Hence, we have attempted to prepare a cost-effective rGO-supported MoO$_3$/Fe$_2$O$_3$ ternary nanocomposite via the hydrothermal route, one of the extensively employed methods for the synthesis of various metal oxide nanostructures [42] due to its high purity with controlled stoichiometry, high crystallinity with controlled morphology, microstructure and narrow particle size distribution [43]. In this article, we discuss the synthesis of MoO$_3$/Fe$_2$O$_3$/rGO ternary composite for effective photocatalytic degradation of a model dye, methylene blue (MB), under visible light illumination.

## 2. Experimental section

### 2.1. Materials and methods

Graphite powder, hydrogen peroxide (H$_2$O$_2$) (30%), hydrochloric acid (HCl) (36.5%), sulfuric acid (H$_2$SO$_4$) (98%), potassium permanganate (KMnO$_4$), sodium nitrite (NaNO$_2$), nitric acid (HNO$_3$) (69%) and sodium hydroxide (NaOH) were purchased from Merck Chemicals Pvt. Ltd, India. Ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) was obtained from Sigma Aldrich Chemicals Pvt. Ltd, India. MB and Triton®X-100 (TX-100) were procured from Rankem Chemicals Pvt. Ltd, India.

### 2.2. Synthesis of MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite

#### Synthesis of α-MoO$_3$ nanobelts

In a typical synthesis, 1.5 g of ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) was dissolved in 39 mL of distilled water with magnetic stirring. 21 mL of 3 mol L$^{-1}$ HNO$_3$ was then added to the above solution and stirred for 5 min after which 100 µL TX-100 was added slowly drop wise to the solution. The obtained transparent solution was transferred and sealed in a Teflon-lined stainless
autoclave with a capacity of 100 mL. The autoclave was heated to 180°C for 20 h in an oven. After completion of 20 h reaction, the autoclave was allowed to cool to room temperature. The obtained precipitate was washed several times with absolute ethanol and double-distilled (2D) water and then dried overnight at 60°C.

**Synthesis of MoO$_3$/Fe$_2$O$_3$ binary nanocomposite**

For the formation of MoO$_3$/Fe$_2$O$_3$ binary nanocomposite, 0.5 g of MoO$_3$ nanobelts powder was added to 50 mL of 0.01 mol L$^{-1}$ Fe(NO$_3$)$_3$·9H$_2$O ethanol solution. After 2 h stirring, the mixture was transferred to a Teflon-lined stainless autoclave with a capacity of 100 mL and sealed. The autoclave was kept at 180°C for 24 h in a temperature controlled oven. After 20 h reaction, the autoclave was allowed to cool to room temperature. Finally, the obtained product was washed with 2D water and dried overnight at 60°C. Pure Fe$_2$O$_3$ was synthesized using the same procedure, but without the addition of MoO$_3$ powder.

**Synthesis of MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite**

Graphene oxide (GO) was synthesized by modified Hummer’s method, a universal method [44]. Briefly, 95 mL of concentrated sulfuric acid was entered into a 500 mL conical flask, which was kept in an ice bath. Two grams of graphite powder and 2g of NaNO$_3$ were added to the above solution. A total of 0.6 g of KMnO$_4$ was then added, and the mixture was stirred continuously for 2 h at room temperature. To the above mixture 95 mL of 2D water was slowly added, followed by the addition of 10 mL of 30% H$_2$O$_2$. Finally, the mixture was filtered and washed with 5% HCl and 2D water until no sulfate ions were detected in the filtrate. The solid was dried in an oven at 70°C for 24 h.

For the synthesis of MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite, the prepared calculated amount of GO was sonicated in 50 mL 2D water for 1 h to generate a clear brown dispersion, and 0.5 g of MoO$_3$/Fe$_2$O$_3$ binary nanocomposite powder was then added. The mixture was stirred vigorously for 2 h to obtain a homogeneous solution. The obtained solution was transferred to a Teflon-lined stainless autoclave with a 100 mL capacity and maintained at 180°C for 24 h in a temperature-controlled oven. After 24 h reaction, the autoclave was allowed to cool to room temperature. Finally, the obtained product was washed and then dried overnight at 60°C.

**2.3. Instrumentation**

The prepared samples were characterized using powder X-ray diffraction (XRD) (D8 Focus, Bruker instrument, Germany) with Cu Ka radiation ($\lambda = 1.5406$ Å), 2θ ranges from 10° to 90° with a scanning speed of 0.02° S$^{-1}$ to identify the crystalline phase of the samples. Fourier transform infrared spectroscopy (FTIR; IFS-66/S, Bruker instrument, Germany) was performed in the transmittance mode, 400–4000 cm$^{-1}$ spectral range with a resolution greater than 0.1 cm$^{-1}$. Surface morphology and elemental analysis were performed using a Quanta FEI 450 scanning electron microscopy (FESEM), a transmission electron microscopy (TEM) (JEOL JEM 2010F microscope) working at 200 kV and an energy dispersive X-ray (EDX) spectrophotometer. The bandgap was calculated using UV-visible absorption spectra from a UV-visible diffuse reflectance spectrophotometer (UV-2600R, Shimadzu, Japan). Raman spectra from 1 to 4000 cm$^{-1}$ were taken using a micro-Raman spectrometer system (ALPHA 300M, WITec, Germany). The photoluminescence (PL) spectra were obtained using a spectrofluorometer (Fluoromax-4, HORIBA, Japan) in order to study the transfer behaviour of photo-generated electrons and holes. A Mettler Toledo TGA/SDTA851e model thermobalance with stake software was used for the thermogravimetric analysis (TGA). The Brunauer–Emmett–Teller (BET) (Quanta chrome Nova 2200 E) surface area was determined from the N$_2$ adsorption-desorption isotherm at 77.3 K.

**2.4. Photocatalytic experiment**

The photocatalytic performance of MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite was evaluated by the degradation of a model organic dye, MB under visible light illumination. The photocatalytic investigation was performed in a Pyrex photoreactor under illumination by a metal halide lamp (400W). Initially, 0.1 g of photocatalyst was added to 100 mL of MB suspension. Before illumination, the solution was stirred magnetically for 10 min in the dark to establish an adsorption–desorption equilibrium of dye solution with catalyst. For every time interval, 5 mL of suspension was collected and centrifuged. The concentration of clear solution was determined using a spectrophotometer (UV-1800, Shimadzu, Japan) of 664 nm a maximum MB absorption.

The photodegradation efficiency was resolute when measuring the absorbance spectra of dye solutions. The degradation efficiency of photocatalytic reaction was calculated using the Equation (1):

$$\text{Degradation efficiency (DE\%)} = \frac{C_0 - C_t}{C_0} \\ = \frac{A_0 - A_t}{A_0} \times 100$$  \hspace{1cm} (1)

where $C_0$ and $A_0$ are the initial concentration and absorbance, $C_t$ and $A_t$ the concentration and absorbance at time $t$, respectively.
absorbance after the photocatalytic reaction with various time intervals (1).

The photocatalytic rate kinetics were followed using Langmuir Hinshelwood kinetics model in Equation (2). From this model, we can observe changes in the concentration of the dye before and after light irradiation (C/C₀), where C₀ and C are the initial and final concentrations of the dye.

\[ C = C_0 e^{-kt} \]  

(2)

### 3. Results and discussion

#### 3.1. XRD spectroscopy

The crystallite size and phase formation were measured by the XRD patterns of the prepared catalysts, MoO₃, Fe₂O₃ and MoO₃/Fe₂O₃, and MoO₃/Fe₂O₃ nanocomposites with various wt% of rGO content are presented in Figure 1. Figure 1(a) shows diffraction peaks at 2θ = 11° and 43°, corresponding to the (002) and (100) reflections, respectively, the resultant phase of GO [45,46]. Figure 1(c) shows the XRD patterns of prepared MoO₃ nanobelts, indicating the presence of sharp diffraction peaks at 2θ = 23.47, 25.80, 27.36, 29.54, 33.73, 35.61, 39.06, 46.30 and 49.34°, which were assigned to the (020), (110), (040), (021), (130), (111), (041), (060), (200) and (002) reflection lines, respectively, and which are closely matched with the reflection lines of α-MoO₃, compared with Standard JCPDS (File No. 05-0508) [47]. This result shows that there is no impurity peak in any XRD pattern, indicating the formation of high purity orthorhombic α-MoO₃ using the hydrothermal approach.

The diffraction peaks of Fe₂O₃ (Figure 1(b)) also match with the standard JPCDS (File No. 33-0664). All the peaks related to the α-MoO₃ crystal phase remain prominently apparent after coupling with Fe₂O₃ (Figure 1(d)), but Fe₂O₃ diffraction peaks appear with very low intensity due to a relatively small amount of Fe₂O₃ present in the MoO₃/Fe₂O₃ binary nanocomposite, which indicates the formation of a two-phase MoO₃/Fe₂O₃ binary nanocomposite. Further, the diffraction peaks of ternary nanocomposites shift slightly towards lower angles with the addition of rGO, as shown in Figure 1(e-i). The intensity of the diffraction peaks decreases, moreover, and the peak width broadens as the amount of rGO increases, indicating interactions of rGO in the ternary nanocomposites. No other diffraction peaks were observed in this pattern, indicating that the pure phase occurred during the synthesis process. The average crystallite size was calculated using the following Debye Scherrer equation (Equation (3)):

\[ D = 0.9λ/(β \cos θ) \]  

(3)

where λ is the wavelength of X-ray radiation and β is the full width at half maximum of the peaks at the diffracting angle θ.

When compared with the binary nanocomposite (31.8 nm) and MoO₃ (44.67 nm), the size of the ternary nanocomposite is seen to be low (22.3 nm), due to incorporation of rGO in the formation of the ternary nanohybrid by hydrothermal-assisted synthesis.

#### 3.2. Scanning electron microscopy

The morphologies and microstructures of the as-prepared metal oxide (MoO₃), binary nanocomposite (MoO₃/Fe₂O₃) and ternary nanocomposite (MoO₃/Fe₂O₃/rGO-5%) were elucidated by FESEM. Figure 2(a, b) reveals a regularly uniform belt-type structure of MoO₃ with a relatively smooth surface. The FESEM images of pure Fe₂O₃ (Figure 2(c, d)) revealed that Fe₂O₃ spherical nanoparticles were agglomerated. Figure 2(e, f) shows FESEM images of the MoO₃/Fe₂O₃ binary nanocomposite. As the MoO₃ nanobelt particles are covered with a large quantity of composite, it is evident that MoO₃ nanobelt-type particles are embedded with Fe₂O₃ to form a new MoO₃/Fe₂O₃ binary nanocomposite, as explained in the XRD results (Figure 1(d)).

Figure 2(g, h) shows the surface morphology of ternary nanocomposite. In the case of ternary nanocomposite, the MoO₃/Fe₂O₃ binary nanocomposites seem to have been completely dispersed with the rGO. The elemental compositions of the MoO₃ nanobelt, MoO₃/Fe₂O₃ binary nanocomposite and MoO₃/Fe₂O₃/ rGO-5% ternary nanocomposite were determined from EDX spectroscopy as shown in Figure 3(a-c). The evidence that the formation of pure-phase ternary nanocomposite by the presence of Mo, Fe, O and C without impurities (Figure 3(c)). The morphology and EDX analysis supported the XRD results, which confirms the purity of the ternary nanocomposite structure.
3.3. Transmission electron microscopy

The structural characteristics of the ternary nanocomposite (MoO$_3$/Fe$_2$O$_3$/rGO-5%) were evaluated using TEM, as shown in Figure 4(a, b). As shown in the results, the widths of the nanobelts were observed to range from 50 nm up to several hundreds of nanometers, and the lengths of the nanobelts increased from several hundreds of nanometers to several tens of micrometers. In particular, these figures show that Fe$_2$O$_3$ nanoparticles are stably present throughout the MoO$_3$ nanobelts to form the MoO$_3$/Fe$_2$O$_3$ binary nanocomposite. MoO$_3$/Fe$_2$O$_3$ binary nanocomposite was well-dispersed on the surface of the rGO layer. These results confirmed the complete formation of MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite.

3.4. Raman analysis

Raman spectroscopy is a powerful tool and an innovative new method for examining reduced graphene oxide-based materials. The characteristic Raman spectra of GO and MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite are shown in Figure 5. In the case of GO (Figure 5(a)), the two peaks observed at 1344.5 and 1594.8 cm$^{-1}$ correspond to the D and G bands, respectively [48]. Here, the appearance of the D band, due to the defects as well as the disordered atomic arrangement caused by k point phonons of the A$_{1g}$ symmetry involving the sp$^2$-carbon atom and G band, can be assigned to the plane vibration E$_{2g}$ phonon of the sp$^2$-carbon atom in the two-dimensional lattice [49,50]. Figure 5(b) shows the Raman spectrum of MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite. It contains both “D” and “G” bands along with bands between 600–1000cm$^{-1}$, 400–600cm$^{-1}$ and below 200cm$^{-1}$ corresponding to the stretching, deformation and lattice
modes of MoO$_3$ [51–54], and fundamental Raman vibrations of Fe$_2$O$_3$ very low-intensity bands were observed. Two characteristic peaks are observed at about 1344.5 cm$^{-1}$ (D band) and 1584.4 cm$^{-1}$ (G band) are observed, suggesting that the structure of rGO is maintained in the composite. In addition, an increased D/G intensity ($I_D/I_G$) ratio from 0.970 to 1.003 in comparison with that of pure GO was also observed, suggesting a decrease in the average size of the sp$^2$ domains during the hydrothermal process, which confirms the reduction of GO to rGO [55]. The efficient reduction of GO to rGO after hydrothermal treatment can also be evidenced by comparison of the XRD and FTIR results.

### 3.5. FTIR spectroscopy

FTIR spectroscopy was used to investigate composites for the existence of oxygen-containing functionalities and changes after impregnation. Figure 6 shows the FTIR spectra of GO, MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-5% nanocomposite. In Figure 6(a) showing the GO FTIR spectrum, the peaks observed at 1717.5 and 1586 cm$^{-1}$ could be attributed to the C = O group and aromatic C = C group of GO. The hydroxyl (-OH) group exhibited a broad band centered at about 3235.5 cm$^{-1}$ [56,57]. The carboxy (C=O), epoxy (C-O) and alkoxy (C-O) group peaks were at 1385.3, 1219.5 and 1038.7 cm$^{-1}$, respectively. Figure 5(b-d) shows MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-5% nanocomposite. The FTIR spectra all have metal oxide stretching band peaks between 1000 and 400 cm$^{-1}$. The FTIR spectrum of the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite reveals that the C = O and O-H group intensities decrease, indicating the removal of oxygen-containing groups through use of the synthesis method and a high-intensity peak observed at 1555.6 cm$^{-1}$ for the C = C bond, results indicating that GO has been reduced to rGO via the hydrothermal process. These results were in good agreement with the results of the XRD and Raman spectra.

### 3.6. Thermogravimetric analysis

TGA was carried out for the synthesized MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-5% nanocomposite shown in Figure 7. Though the observed trends of weight loss for all the samples appear somewhat similar, a close look at the curves clearly indicates that their magnitude of weight loss is dependent not only on the temperature difference but also on the composition. The TGA curve (a) of MoO$_3$ shows a total weight loss of 4.5%, and the curve (b) of the MoO$_3$/Fe$_2$O$_3$ binary nanocomposite shows a total weight loss of 6.5% due to loss of total absorbed water molecules. The TGA curve (c) of the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite shows a total weight loss of 10.5%. However, the weight loss of the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite sample was broadly characterized in three stages in the temperature ranges from 25°C to 100°C, 100°C to 300°C and 300°C to 800°C, suggesting that TGA curves of the present samples were recorded for synthesized

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**Figure 5.** Raman spectra of (a) graphene oxide and (b) MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite.

**Figure 6.** FT-IR spectra of (a) GO, (b) MoO$_3$, (c) MoO$_3$/Fe$_2$O$_3$ and (d) MoO$_3$/Fe$_2$O$_3$/rGO-5%.

**Figure 7.** TGA curves of (a) MoO$_3$, (b) MoO$_3$/Fe$_2$O$_3$ and (c) MoO$_3$/Fe$_2$O$_3$/rGO-5%.
samples but not during the sample synthesis. Of particular, the composite shows only a 3.2% change in the first stage of weight loss, whereas the second and third stages showed additional weight losses of about 5.2% and 2.1%, respectively.

The observed variations in the TGA curve (c) of the sample MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite can be interpreted as follows. For the sample, the first stage of weight loss corresponds to the evaporation of adsorbed water while the second stage of weight loss, which is considered the major weight loss, is attributed more to the oxidation, reduction, crystallization, recrystallization and removal of oxygen-containing functional groups present after the hydrothermal process as well as to dehydroxylation of the remaining hydroxides. The onset of further weight loss for the third stage at 300°C to 800°C was smaller in magnitude due to pyrolysis of the carbon skeleton [58]. Nevertheless, it can also be inferred from the TGA curve of the composite that the amount of rGO coating the surface of the nanoparticles might lead to inhibiting the particle growth and result in smaller particles of the sample.

### 3.7. UV–Vis diffuse reflectance spectroscopy

The absorbance properties of the prepared catalysts were measured using UV–Vis diffuse reflectance spectroscopy (UV-DRS). Figure 8(a–e) displays the UV–Vis diffuse reflectance spectra of MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$-bearing rGO loaded (with 1%, 5% and 10%) ternary nanocomposites. The bandgap energy ($E_g$) of the catalyst can be calculated using the following formula [59]:

$$E_g (eV) = \frac{1240}{\lambda}$$

where $E_g$ is bandgap energy and $\lambda$ is the wavelength (nm) corresponding to the absorption edge.

![Figure 8. UV-vis DRS spectra of (a) MoO$_3$, (b) MoO$_3$/Fe$_2$O$_3$, (c) MoO$_3$/Fe$_2$O$_3$/rGO-1%, (d) MoO$_3$/Fe$_2$O$_3$/rGO-5% and (e) MoO$_3$/Fe$_2$O$_3$/rGO-10%.](image)

The bandgap energies were calculated on the basis of corresponding absorption edges and by extrapolating the sharp horizontal rising portions of the curves, while defining the edges as energies of intersection. The bandgap energies ($E_g$) of pure MoO$_3$, MoO$_3$/Fe$_2$O$_3$ nanocomposite and MoO$_3$/Fe$_2$O$_3$/rGO-(1, 5 and 10%) ternary nanocomposites were calculated are 2.88 (430 nm), 1.76 (704 nm), 1.70 (729 nm), 1.65 (751 nm) and 1.68 eV (738 nm), respectively. On the other hand, the absorption edge of the binary nanocomposite (MoO$_3$/Fe$_2$O$_3$), as shown in Figure 8(b), shifts to the more visible range and has a higher absorption intensity than pure MoO$_3$, indicating effective surface hybridization between these components [60,61]. With increase in rGO loading, ternary nanocomposite reaches a maximum absorption edge (751 nm) of 5% rGO, and then decreases for 10% rGO (738 nm). This shows that the interaction between Mo–O–C and Fe–O–C takes place in the ternary nanocomposite. A similar observation was reported earlier for semiconductors coupled with GO [62,63]. Thus, it can be confirmed that composite transition metal oxides and synergies with rGO were efficient for visible-light response and enhancement of the photocatalytic activity.

### 3.8. BET surface area analysis

The specific surface areas of as-prepared photocatalysts were evaluated using N$_2$ adsorption–desorption analysis. Because the photocatalytic processes of nanocomposite are generally surface-controllable processes, a large surface area can enhance the photocatalytic activity of nanocomposite due to the large number of active sites on the surface for adsorption of reactant molecules. Table 1 shows typical N$_2$ adsorption–desorption isotherms for MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO with 1%, 5% and 10% rGO-containing ternary nanocomposites. Based on these results, the specific surface areas of pure MoO$_3$ and binary nanocomposite (MoO$_3$/Fe$_2$O$_3$) are 9.0 and 18.1 m$^2$/g, respectively, and that of the ternary nanocomposite (MoO$_3$/Fe$_2$O$_3$/rGO-5%) is 26.4 m$^2$/g due to their high specific surface area compared to other ternary nanocomposites. It is clear that the specific surface area of ternary nanocomposite increases due to exfoliation and cross-linking points between rGO and the binary composite (MoO$_3$/Fe$_2$O$_3$ nanobelts) up to an optimal level (5%)

| S. No | Catalyst | Specific surface area (m$^2$/g) |
|-------|----------|---------------------------------|
| 1     | MoO$_3$  | 9.0                             |
| 2     | MoO$_3$/Fe$_2$O$_3$ | 18.1                      |
| 3     | MoO$_3$/Fe$_2$O$_3$/rGO-1% | 25.0                       |
| 4     | MoO$_3$/Fe$_2$O$_3$/rGO-5% | 26.4                       |
| 5     | MoO$_3$/Fe$_2$O$_3$/rGO-10% | 23.6                       |

![Table 1. Specific surface areas of the as-prepared catalysts.](image)
[64]. In MoO$_3$/Fe$_2$O$_3$/rGO-10% ternary composite, however, the specific surface area decreases to 23.6 m$^2$/g owing to adequate exfoliation of the rGO sheets, resulting in wrapping and folding over of the MoO$_3$/Fe$_2$O$_3$ nanobelts. The ternary nanocomposite (MoO$_3$/Fe$_2$O$_3$/rGO-5%) has higher specific surface area, thus it is more photocatalytically active, because the reactant molecules adsorb more on surface of the catalyst and larger numbers of molecules react with photoactive radicals in the presence of visible light.

3.9. PL spectra

The production of ·OH radicals on the surface of the catalyst was detected by the PL method using terephthalic acid as a probe molecule, which readily reacted with ·OH radicals to produce a highly fluorescent (2-hydroxyterephthalic acid) product. The PL intensity of 2-hydroxyterephthalic acid is proportional to the amount of ·OH produced on the surface of a catalyst [65,66]. Figure 8 shows the change with irradiation time in PL emission spectrum for a MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite excited at 315 nm in terephthalic acid solution (0.5 mM terephthalic acid in 5 mM NaOH solution) is determined using a spectrofluorometer.

An increase in PL intensity at approximately 425 nm is observed under 60 min visible light irradiation as shown in Figure 9(b). No increase in PL intensity is observed, however, in the absence of visible light on the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite as shown in Figure 9(a). This can be attributed to the large numbers of unpaired electrons and holes on the surface of the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite, which adsorb O$_2$ and H$_2$O to form more ·OH radicals. This result indicates that fluorescence stem from the chemical reaction between terephthalic acid and ·OH is formed on the MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite to create a water interface through a photocatalytic reaction. The ternary nanocomposite (MoO$_3$/Fe$_2$O$_3$/rGO-5%) served as a benign photocatalyst due to the faster formation rate of ·OH radicals, leads to higher photocatalytic activity.

3.10. Photocatalytic activity

The photocatalytic performance of MoO$_3$, Fe$_2$O$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-(1%, 3%, 5%, 7% and 10% of rGO loading) catalysts were examined by degradation of MB aqueous solution under visible light illumination. Figure 10(a) shows the evolution of time-dependent UV-visible absorption spectra of degradation of MB dye by MoO$_3$/Fe$_2$O$_3$/rGO-5%

![Figure 9](image-url) PL spectra of terephthalic acid solution containing MoO$_3$/Fe$_2$O$_3$/rGO-5%: (a) before irradiation; and (b) after irradiation of 60 min.

![Figure 10](image-url) (a) UV-visible absorption spectral changes of MB during photocatalytic degradation by MoO$_3$/Fe$_2$O$_3$/rGO-5%; (b) Photocatalytic degradation of MB using the prepared photocatalysts under visible light illumination; (c) Kinetic photocatalytic degradation plot for MB using the prepared photocatalysts under visible light illumination.
nanocomposite under visible light illumination for 60 min, revealing that the maximum absorption peak of MB at 664 nm decreases gradually with increases in the irradiation time. All the synthesized photocatalysts degraded the MB under visible light illumination at different time intervals, which confirms that all the catalysts were photocatalytically active. Among the different catalysts, photocatalytic degradation of the MB solution maximum absorption peak at 664 nm (Figure 10(a)) was almost eliminated (The blue colored reaction solution was almost completely converted into a colorless solution) after 60 min under visible light illumination. The observed changes in the concentration of MB and the time-dependent degradation ratios ($C/C_0$) of MoO$_3$, Fe$_2$O$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-(1%, 3%, 5%, 7% and 10%) catalysts are presented in Figure 10(b). According to the Langmuir-Hinshelwood kinetics model, moreover the function of ln($C/C_0$) versus the reaction time (t) displayed a linear relationship, as shown in Figure 10(c).

The corresponding first-order kinetic rate constant (k) and the regression coefficient ($R^2$) of MB were calculated as listed in Table 2. The photocatalytic degradation process of MB solution with photocatalysts under visible light illumination follows the first-order kinetic rate constant shown in Figure 11. After irradiation of the MB solution for 60 min, the photocatalytic degradation efficiencies (DE%) of all the catalysts were calculated, as presented in Figure 12. The Figure 12 shows the 45.04%, 74.09%, 80.78% and 87.86%, 93.37%, 99.47%, 93.90% and 90.88% DE% of MB for Fe$_2$O$_3$, MoO$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$ ternary nanocomposite containing 1%, 3%, 5%, 7% and 10% rGO, respectively. These results suggest that MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite exhibited a higher DE% (99.47%) than the other catalysts; hence they have higher photocatalytic activity. Based on the photocatalytic activity results, MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite offers a greater potential for photocatalytic activity than MoO$_3$, Fe$_2$O$_3$, MoO$_3$/Fe$_2$O$_3$ and MoO$_3$/Fe$_2$O$_3$/rGO-(1%, 3%, 7% and 10%) ternary nanocomposites. Ternary nanocomposites (with wt % changes of rGO loading) showed better photocatalytic activity than MoO$_3$/Fe$_2$O$_3$, which has higher photocatalytic activity than MoO$_3$ and Fe$_2$O$_3$. Well-maintained rGO loading of ternary nanocomposites increases the photocatalytic efficiency up to the optimum level of 5% rGO. Further increases in rGO loading (7wt% and 10wt%) were observed to decrease the DE% by reducing the light absorption in the suspension during the photocatalytic reaction as a result of increased catalyst opacity. The increase in the photocatalytic activity of MoO$_3$/Fe$_2$O$_3$/rGO ternary nanocomposite was based on the following features: the MoO$_3$ nanobelts morphology, a high surface area and strong absorption in the visible region; and heterojunction of the ternary nanocomposite and enhanced charge separation efficiency and suppression of the electron hole pair recombination rate in the ternary nanocomposite. The migration of charge carriers may increase at the interface of two metal oxides via a synergetic interaction, moreover, through the formation of heterojunction in the ternary nanocomposite. On the other hand,

![Figure 11](image1.png)

**Figure 11.** First-order rate constant for photocatalytic degradation of MB with photocatalysts under visible light illumination: (a) Fe$_2$O$_3$, (b) MoO$_3$, (c) MoO$_3$/Fe$_2$O$_3$, (d) MoO$_3$/Fe$_2$O$_3$/rGO-1%, (e) MoO$_3$/Fe$_2$O$_3$/rGO-3%, (f) MoO$_3$/Fe$_2$O$_3$/rGO-5%, (g) MoO$_3$/Fe$_2$O$_3$/rGO-7% and (h) MoO$_3$/Fe$_2$O$_3$/rGO-10%.

![Figure 12](image2.png)

**Figure 12.** The degradation efficiency of MB induced by (a) Fe$_2$O$_3$, (b) MoO$_3$, (c) MoO$_3$/Fe$_2$O$_3$, (d) MoO$_3$/Fe$_2$O$_3$/rGO-1%, (e) MoO$_3$/Fe$_2$O$_3$/rGO-3%, (f) MoO$_3$/Fe$_2$O$_3$/rGO-5%, (g) MoO$_3$/Fe$_2$O$_3$/rGO-7% and (h) MoO$_3$/Fe$_2$O$_3$/rGO-10%.

![Table 2](image3.png)

**Table 2.** First-order kinetic rate constant (k) and regression coefficient ($R^2$) of MB under visible light illumination.

| Catalyst          | $k \times 10^{-3}$ in min$^{-1}$ | $R^2$   |
|-------------------|---------------------------------|--------|
| MoO$_3$           | 0.334                           | 0.9670 |
| Fe$_2$O$_3$       | 0.162                           | 0.9534 |
| MoO$_3$/Fe$_2$O$_3$| 0.402                           | 0.9708 |
| MoO$_3$/Fe$_2$O$_3$/rGO-1% | 0.518             | 0.9455 |
| MoO$_3$/Fe$_2$O$_3$/rGO-3% | 0.658             | 0.9582 |
| MoO$_3$/Fe$_2$O$_3$/rGO-5% | 0.878             | 0.9135 |
| MoO$_3$/Fe$_2$O$_3$/rGO-7% | 0.704             | 0.9464 |
| MoO$_3$/Fe$_2$O$_3$/rGO-10% | 0.588             | 0.9695 |
the addition of rGO to binary nanocomposite results in an increase in the surface area of the ternary nanocomposite, which helps to make a longer number of active sites available on the catalyst surface and, therefore, enables it to accommodate more reactant molecules, resulting in greater photocatalytic degradation of MB dye. MoO$_3$/Fe$_2$O$_3$/rGO-5% ternary nanocomposite exhibits a longer high surface area than the other catalysts and a higher level of photocatalytic degradation, as shown by the results in Table 1. In addition, these ternary nanocomposites have stronger absorption properties in the visible region than MoO$_3$, Fe$_2$O$_3$, and MoO$_3$/Fe$_2$O$_3$. This extended and strengthened absorption facilitates the degradation of more reactant molecules through the formation of more photoinduced charge carriers under visible light irradiation [67].

### 3.11. Reactive oxygen species assay

Light enhances the generation of reactive oxygen species such as hydroxyl (‘OH) and superoxide (‘O$_2^-$) radicals due to the interaction of semiconductor nanoparticles in an aqueous medium, which has been shown to be an essential process for photocatalytic degradation of dye [68,69]. In the reaction medium, the generation of (‘O$_2^-$) and (‘OH) radicals was determined by treatment with their respective scavengers, p-benzoquinone and DMSO (dimethylsulfoxide) [70], comprising the MB dye solution and MoO$_3$/Fe$_2$O$_3$/rGO-5% as photocatalyst.

In a typical reaction mixture, the (‘OH) radicals were determined by treatment with DMSO as a quencher for degradation of MB dye solution was treated with MoO$_3$/Fe$_2$O$_3$/rGO-5% (0.1 g) ternary nanocomposite (Figure 13.A(b)). A control experiment was conducted in the absence of DMSO (Figure 13.A(a)). After equilibrating the reaction mixture in the dark for 10 min followed by exposure to visible light, the kinetics of dye degradation inhibition were studied by monitoring the intensity of the UV-visible absorption spectra of the dye.

Similarly, the methodology for (‘OH) radicals using p-benzoquinone as a scavenger due to the poor water solubility of p-benzoquinone. Initially, the commercially procured p-benzoquinone was recrystallized from ethanol and then dissolved in ethanol (98%), which was mixed with the MB dye solution prepared in ethanol and water ratio was 1:9. MoO$_3$/Fe$_2$O$_3$/rGO-5% (0.1 g) nanoparticles were added to MB dye solution mixed with p-benzoquinone and equilibrated in the dark for 10 min and then exposed to visible light. Since ethanol evaporates faster than water, it was necessary to maintain the ethanol and the water ratio in the dye solution throughout the period of the kinetic study by adding appropriate volumes of ethanol. The inhibition of MB dye degradation by the addition of p-benzoquinone was determined from a kinetic study (Figure 13.B(a) and (b)), as described earlier.

### 3.12. Proposed mechanism

A proposed mechanism for improved efficiency of photocatalytic degradation of MoO$_3$/Fe$_2$O$_3$/rGO
ternary nanocomposite in the presence of visible light irradiation is presented in the schematic diagram 4. The MoO₃/Fe₂O₃/rGO ternary nanocomposite is maintained under visible light illumination; initially, MoO₃/Fe₂O₃ undergoes a charge separation process that leads to movement of electrons from the valence band (VB) to the conduction band (CB) and leaves a hole in the VB. Due to the formation of heterojunction, the generated photoelectrons in the CB of Fe₂O₃ are transferred to the CB of MoO₃. Meanwhile, the excited holes in the VB of the MoO₃ nanobelts are transferred to the VB of Fe₂O₃. Finally, the generated photoelectrons are captured by the rGO sheets through semiconductor carbon heterojunction. The rGO sheets have a large surface area rich in electronic conductivity, which enhances the easy transport of generated photoelectrons to the composite surface, thus inhibiting the recombination between the photoinduced electrons and holes. This results in dramatically enhanced generated photo charge separation efficiency in the ternary nanocomposite. These separated electrons and holes react directly with oxygen and water to generate highly reactive superoxide radicals (’O₂−) and hydroxyl radicals (’OH). These energetic reactive radicals consequently react with surface-adsorbed MB molecules and degrade them into small intermediate molecules, such as CO₂ and H₂O. Based on the earlier explanation, the mechanism for photocatalytic degradation of dye in the presence of MoO₃/Fe₂O₃/rGO ternary nanocomposite under visible light irradiation can be shown by the following equations:

\[
\begin{align*}
\text{MoO}_3/\text{Fe}_2\text{O}_3 + h\nu & \rightarrow \text{MoO}_3/\text{Fe}_2\text{O}_3(\text{e}^-) + \text{MoO}_3/\text{Fe}_2\text{O}_3(\text{h}^+) \\
\text{MoO}_3/\text{Fe}_2\text{O}_3(\text{h}^+) + \text{H}_2\text{O} & \rightarrow \text{MoO}_3/\text{Fe}_2\text{O}_3 + \text{OH} + \text{H}^+ \\
\text{MoO}_3/\text{Fe}_2\text{O}_3(\text{e}^-) + \text{rGO} & \rightarrow \text{rGO}(\text{e}^-) + \text{MoO}_3/\text{Fe}_2\text{O}_3 \\
\text{rGO}(\text{e}^-) + \text{O}_2 & \rightarrow \text{rGO} + \text{O}_2^{-2} \\
\text{H}_2\text{O} + \text{O}_2^{-2} & \rightarrow \text{HO}_2^* + \text{OH}^- \\
2\text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{O}_2^{-2} & \rightarrow \text{OH}^- + \text{OH} + \text{O}_2 \\
\text{OH}/\text{O}_2^{-2}/\text{HO}_2^* & \rightarrow \text{dyes} \rightarrow \text{Degradation products}
\end{align*}
\]

Based on the experimental conditions, MoO₃/Fe₂O₃/rGO-5% ternary nanocomposite exhibits the highest photocatalytic activity among all the prepared catalysts.

4. Conclusions

In conclusion, we have synthesized a series of MoO₃/Fe₂O₃/rGO ternary nanocomposites using an in situ hydrothermal method for the photocatalytic degradation of MB dye under visible light illumination. In a hybrid structure, the enormous surface area of rGO sheets not only inhibits the aggregation of Fe₂O₃ in MoO₃/Fe₂O₃ binary composite but also assists in enhancing the degradation of MB dye molecules, which eventually offer more photocatalytic reaction sites. Moreover, the as-synthesized MoO₃/Fe₂O₃/rGO-5% ternary nanocomposite exhibited excellent performances in the complete photocatalytic degradation of MB in aqueous solution under visible light illumination. After incorporation with different rGO loads, they displayed enhanced photocatalytic activity up to the saturation level and enhanced light-harvesting efficiency.

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Disclosure statement

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Highlights

1. Successful synthesis of MoO₃/Fe₂O₃/rGO ternary nanocomposite.
2. Easy preparation of ternary nanocomposite by in situ hydrothermal-assisted synthesis.
3. Complete degradation of the dye pollutant Methylene blue (MB) in 60mins in the presence of visible light by MoO₃/Fe₂O₃/rGO.
4. Improved photocatalytic activity towards photocatalytic degradation of MB under visible light illumination as compared with pure MoO₃, Fe₂O₃, and MoO₃/Fe₂O₃ binary nanocomposite.

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