CHAPTER 6

PREPARATION AND CHARACTERIZATION OF LaFeO$_3$/rGO NANOCOMPOSITES WITH ENHANCED VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY

6.1 INTRODUCTION

In recent years, visible-light-driven photocatalysts have been developed for efficient utilization of solar energy to address the increasing environmental pollution and energy problems. To date, a large number of metal oxides as photocatalyst have been explored for the purpose of efficient degradation of harmful organic substances and hydrogen production through decomposing water. In particular, the TiO$_2$ photocatalyst is widely employed in the environmental cleaning by degrading organic pollutants and hydrogen production by decomposing water, due to their excellent photochemical stability, low cost, and non-toxicity (Ma et al 2013, Tian et al 2009, Yang et al 2006). However, for practical applications, TiO$_2$ is not a good candidate in the visible light region, because it only absorbs ultraviolet light of no longer than 387 nm for the anatase phase and 413 nm for the rutile phase. From the viewpoint of using solar energy, it is of great interest to develop efficient visible-light photocatalysts for the photodegradation of organic pollutants.

Recently perovskite-type oxide materials have attracted considerable attention because of their useful application in many fields (Koferstein et al 2014, Liu et al 2011). To maximize the use of sunlight, a new type of photocatalyst with a perovskite structure has been recently used
as a highly effective photocatalyst in the visible region (Hu et al 2014, Yang et al 2013, Tang et al 2013, Liu et al 2013). LaFeO$_3$ is one of the important perovskite material widely reported for various applications including solid oxide fuel cells (Fujii et al 2011, Li et al 2011, Liu et al 2011), sensors (Farhadi 2009, Feng et al 2011), catalysts (Fujii et al 2011, Li et al 2011, Liu et al 2011, Farhadi et al 2009, Feng et al 2011) and magnetic materials (Abazari et al 2013, Wang et al 2006) etc. In recent years, the photocatalyst LaFeO$_3$ has attracted considerable attention because of its high catalytic activity, low cost, and environmental friendliness.

Graphene an attractive carbon material, is promising for enhancing photocatalytic activity in the recent years because of its tremendous adsorption capacity, strong mechanical stability, high chemical stability, good electrical conductivity and large specific surface area therefore it has drawn a great deal of research interest for various applications (Liu et al 2011, Zhan et al 2011, Hu et al 2012, Wang et al 2012, An et al 2013, Rao et al 2009). Development of novel nanocomposites with enhanced photocatalytic behaviour has received increasing attention recently. Now a day, combining of graphene with other nanoparticles were reported to develop novel nanocomposites such as graphene-based metal nanoparticles and metal oxides. Hu et al. reported the synthesis and photocatalytic properties of LaMnO$_3$–graphene nanocomposites. Wang et al. obtained promotional effect of graphite oxide on surface properties and catalytic performance of LaSrMnO$_3$ for methane combustion. Li et al reported the hydrothermal preparation, characterization and enhanced properties of reduced graphene-BiFeO$_3$ nanocomposite. Liu et al. received enhanced photocatalytic activity of Nickel ferrite/GO for degradation of dyes under visible light. Zheng et al. received the enhanced microwave electromagnetic properties of Fe$_3$O$_4$–graphene nanosheet composites. So, it is of great interest to study the graphene complex oxide nanocomposites, such as LaFeO$_3$/rGO systems.
Therefore, in this present work, LaFeO$_3$ was combined to graphene. The electronic migration rate of graphene is extremely high. The recombination of electron and hole gets decreases this improves the photocatalytic efficiency. Hence in the present study synthesis of LaFeO$_3$/rGO was carried out through hydrothermal method and the photocatalytic behaviour of the composite has been investigated for the first time. Finally, the photocatalytic activity was measured and the influence of carbon on the photocatalytic activity of LaFeO$_3$/rGO nanocomposites was also investigated by decomposing MO solution.

6.2 EXPERIMENTAL PROCEDURE

6.2.1 Preparation of GO

GO was synthesized using a modified Hummers method (Zhan et al 2011). The procedure details are as follows. Initially 1.0 g of powder graphite flakes and 0.5 g of sodium nitrate was added to 23 mL of 98 % sulfuric acid while stirring. The compound was mixed in a 250 mL beaker that was cooled to 10 °C in an ice bath. While maintaining vigorous stirring, 3.0 g of potassium permanganate was added to the suspension, and stirring was maintained for 3 h. After that, the ice bath was removed, and the temperature of the suspension was increased to 35 °C and maintained for 45 min. Then, 45 mL of distilled water was added slowly dropped into the paste, causing violent effervescence and an increase in temperature to 98 °C. The diluted brown color suspension was maintained at this temperature for 15 min. Then, approximately 140 mL of warm water was added slowly dropped into the paste, causing violent effervescence and an increase in temperature to 98 °C. The diluted brown color suspension was maintained at this temperature for 15 min. Then, approximately 140 mL of warm water was added to the suspension for further dilution and then treated with 10% of H$_2$O$_2$ to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. Upon treatment with H$_2$O$_2$, the suspension turned bright yellow color. The suspension was centrifuged, yielding a yellow–brown paste. The suspension was centrifuged, yielding a yellow–brown paste. Finally, the mixture was
filtered and washed with HCl solution to remove metal ions followed by deionized water to remove the acid, resulting in GO.

### 6.2.2 Preparation of LaFeO$_3$/rGO

A stoichiometric amount (1:1) of lanthanum (III) nitrate hexahydrate [La(NO$_3$)$_3$.6H$_2$O] and iron (III) nitrate nanohydrate [Fe(NO$_3$)$_3$.9H$_2$O] were dissolved in 50 ml of double distilled water under magnetic stirring. Then GO was added to above solution, followed by ultrasonic treatment for about 30 min until GO was well dispersed in the solution. The molar amount of citric acid added was equal to the total molar amount of metal nitrate in the solution. The solution was continuously stirred for 5 h at room temperature. Ammonia solution was slowly added to adjust the pH 9.2 and also to stabilize the nitrate-citrate solution. After stirring for 3 h at room temperature, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of about 70 mL, the autoclave was sealed and heated at 180 °C for 20 h and then cooled naturally to room temperature. The obtained precipitate was collected and washed with deionized water and anhydrous ethanol several times and then dried in air at 100 °C followed by calcination at 800 °C for 6 h at both N$_2$ and air atmosphere to obtain LaFeO$_3$/rGO powder. For comparison, LaFeO$_3$ were prepared by a similar process without using GO.

### 6.3 CHARACTERIZATION STUDIES

The as-synthesized sample was first subjected to thermal analysis in order to find the decomposition, stability and phase formation of the material using SII TG/DTA 6300 thermal analyzer. The TGA curve was recorded in the range from 27 to 900 °C with a heating rate of 20 °C/min under nitrogen atmosphere. Powder X-Ray diffraction analysis (XRD) was carried out for the annealed samples with a GE Inspection Technologies 3003TT model.
The X-ray diffraction pattern was obtained in the 2θ range from 5° to 70° and was inspected using JCPDS data to identify the crystallographic phases. The FT-IR measurements have been performed in the potassium bromide mode (KBR) using the model 6300 FT-IR spectrophotometer. The vibrational characteristics of the LaFeO₃ powders were investigated using Renishaw invia Raman microscope, Leica DMLM, RL663 laser. The surface morphology of synthesized samples and elemental presence has been studied by high resolution scanning electron microscopy (HRSEM) using FEI Quanta FEG 200 microscope operated at 20 kV. The particles size and morphology of the synthesized sample has been studied by high resolution transmission electron microscopy (HRTEM) using Tecnai G2 model T-30 s-twin electron microscope with an accelerating voltage of 300 kV. The atomic force microscopy (AFM) measurements of the sample have been performed in non-contact mode at room temperature using XE 70 Park system. X-ray photoelectron spectroscopy (XPS) has been done to confirm the oxidation state of the elements present in the sample. The XPS data were collected using Omicron Nanotechnology instrument with a binding energy resolution of 0.7 eV. The optical absorption study of the synthesized sample has been carried out in the range of 200-800 nm using Cary 5E high resolution spectrophotometer. The vibrating sample magnetometer (VSM) measurements of the samples were recorded at room temperatures (300 K) using Lakeshore VSM 7410.

6.4 RESULTS AND DISCUSSION

6.4.1 Thermal Studies

The optimizing annealing temperature of the synthesized powders were carried out by TG analysis and shown in Figure 6.1. Generally for GO, there are two major weight loss was occurred with the increase of...
temperature. The initial weight loss of 16 % occurs between room temperature and 150 °C could be attributed to the removal of absorbed water. The second significant weight loss of about 25 % at around 200 °C indicated the removal of COOH groups (Metin et al 2014, Guo et al 2013). This result suggests that the graphite flakes were successfully oxidized into the thin layered GO structure.

TGA curve of LaFeO$_3$ and LaFeO$_3$/rGO shows four weight loss segments. It can be seen that the first and last segment are due to the elimination of water and the crystallization process of the material. The second significant weight loss observed between 200 to 310 °C is mainly due to the decomposition of organic compounds like C–N, C–H and C=O. The third weight loss was up to ~500 °C may be due to the decomposition of nitrates (NO$_3^-$). There is no further weight loss was observed after ~700 °C which confirms the possible formation of metal oxide phase of perovskite LaFeO$_3$. With respect to above result the sample was annealed at 800 °C.

![Figure 6.1 TGA curve of (a) LaFeO$_3$ and LaFeO$_3$/rGO (b) GO sample](image)

Figure 6.1 TGA curve of (a) LaFeO$_3$ and LaFeO$_3$/rGO (b) GO sample
6.4.2 X-ray Diffraction Studies

The X-ray diffraction patterns of as-prepared LaFeO$_3$, GO, rGO and LaFeO$_3$/rGO nanocomposites annealed at both air and N$_2$ atmosphere are shown in Figure 6.2. The obtained LaFeO$_3$ sample consists of orthorhombic phase and indexed on basis of JCPDS file No. 37-1493. The obtained XRD pattern of GO nanosheets exhibit a (002) diffraction peak at 10.5° which confirms the formation of GO (Qu et al 2012, Ji et al 2014, Luo et al 2012). The XRD peak further shows that all the diffraction peaks of LaFeO$_3$/rGO nanocomposites annealed at air and N$_2$ atmosphere can be assigned similar to a single phase LaFeO$_3$ belonging to orthorhombic distorted perovskite LaFeO$_3$ phase. However, no typical diffraction peaks of GO (002) were observed in the LaFeO$_3$/rGO nanocomposites annealed at both air and N$_2$.
atmosphere, which may be due to the low amount and relatively low diffraction intensity of GO present in the composites.

6.4.3 FT-IR Studies

![FT-IR spectra of LaFeO₃, GO and LaFeO₃/rGO sample](image)

Figure 6.3 FT-IR spectra of LaFeO₃, GO and LaFeO₃/rGO sample

In order to study the formation of LaFeO₃, GO and LaFeO₃/rGO nanocomposites, the as-prepared samples were characterized by FT-IR spectroscopy and the results are shown in Figure 6.3. The FT-IR spectra of GO shows a broad and strong peak at around 3410 cm⁻¹ corresponding to the stretching vibrations of hydroxyl (OH) groups. The additional peaks at 1040 cm⁻¹, 1224 cm⁻¹, 1362 cm⁻¹ and 1727 cm⁻¹ corresponds to C–O stretching, C–OH stretching, C–O–H bending and C–O stretching vibrations of carboxyl (COOH) groups. The peak at 1619 cm⁻¹ is related to aromatic C–C indicating the hybrid sp² structure of grapheme (Guo et al 2013, Qu et al 2012, Ji et al
2014, Luo et al 2012, Wang et al 2010). The peak at 1550 cm$^{-1}$ is attributed to the skeletal vibration of graphene sheets.

For pure LaFeO$_3$ the sharp absorption band at 555 cm$^{-1}$ attributed to B–O (Fe-O) stretching vibration, being characteristics of the octahedral BO$_6$ groups in the perovskite (ABO$_3$) compound, which is commonly observed in the region 500–700 cm$^{-1}$ (Feng et al 2011, Abazari et al 2013). For the LaFeO$_3$/rGO nanocomposites annealed at N$_2$ atmosphere both the GO and LaFeO$_3$ vibrations are occurred which confirms the formation of LaFeO$_3$/rGO nanocomposites. Further it was found from spectra that the sample annealed at N$_2$ atmosphere has strong stretching vibrations at 1727 cm$^{-1}$ and 1619 cm$^{-1}$ when compared with the sample prepared by air atmosphere. Hence the presence of carbon in the N$_2$ atmosphere is high when compared with air atmosphere annealed sample.

6.4.4 Raman Studies

Figure 6.4 shows the Raman spectra of LaFeO$_3$, GO and LaFeO$_3$/rGO nanocomposites. The bands at around 434, 628, 960, 1135 and 1320 cm$^{-1}$ are related to LaFeO$_3$ which was similar to the previous report (Popa et al 2002, Wang et al 2006). The bands at 434 and 1135 cm$^{-1}$ were assigned to the one phonon scattering, while 1320 cm$^{-1}$ were assigned to the two phonon scattering. The band at 630 cm$^{-1}$ band in LaFeO$_3$ was assigned to impurity scattering. The G band arises from the zone center E$_{2g}$ mode, corresponding to ordered sp$^2$ bonded carbon, and the D band is as a breathing mode of k-point phonons of A$_{1g}$ symmetry, which is attributed to local defects and disorders, particularly the defects located by the edges or in samples (Hu et al 2014). The presence of D and G band at 1345 and 1595 cm$^{-1}$ in the spectrum of graphene oxide indicates the ordered sp$^2$ structure. The LaFeO$_3$/rGO nanocomposites annealed at N$_2$ atmosphere exhibits both LaFeO$_3$ bands and GO bands. The LaFeO$_3$/rGO nanocomposite annealed at
air atmosphere spectrum was similar to that of LaFeO$_3$ sample. The result illustrates that the GO maintains the original structure in LaFeO$_3$/rGO nanocomposites annealed at N$_2$ atmosphere.

![Figure 6.4 Raman spectra of LaFeO$_3$, GO and LaFeO$_3$/rGO sample](image)

6.4.5 **High Resolution Scanning Electron Microscopy Studies**

Surface morphology of LaFeO$_3$ samples were characterized by HRSEM and the micrographs were shown in Figure 6.5. Low and high magnification of HRSEM images of the prepared LaFeO$_3$ sample shows narrow size distribution at a large scale. In addition, it was noticed that the hydrothermal synthesis method produced highly monodispersed LaFeO$_3$ nanospheres with average size of about 45 nm. Further no other impurity particles and aggregates are detected.
Figure 6.5 HRSEM images of LaFeO$_3$ nanospheres

Figure 6.6 shows HRSEM images of prepared graphene oxide nanosheets. Graphene clearly showed its nano-sheet structure and its layered platelets were composed of curled nanosheets.

Figure 6.7 shows the LaFeO$_3$/rGO sample annealed at N$_2$ atmosphere it shows that surface of curled GO nanosheets is packed densely with LaFeO$_3$ nanoparticles, which displays a good combination between GO and LaFeO$_3$. The GO nanosheets act as bridges for different LaFeO$_3$ nanoparticles, which is beneficial for the separation of photo-generated carriers and enhances the photocatalytic performance.
Figure 6.6 HRSEM images of GO Nanosheets

Figure 6.7 HRSEM images of LaFeO$_3$/rGO nanocomposite annealed at N$_2$ atmosphere
Figure 6.8 shows the LaFeO$_3$/rGO nanocomposites annealed at air atmosphere it is observe from the image that there is only a distribution of LaFeO$_3$ nanoparticles. Hence there is no possible of interaction between the GO nanosheets and LaFeO$_3$ nanoparticles therefore the result of LaFeO$_3$/rGO nanocomposites annealed at air atmosphere is similar to that of LaFeO$_3$ nanoparticles.

![HRSEM images of LaFeO$_3$/rGO nanocomposite annealed at air atmosphere](image)

**Figure 6.8**  HRSEM images of LaFeO$_3$/rGO nanocomposite annealed at air atmosphere

### 6.4.6 Elemental Studies

Figure 6.9 shows EDS spectra of GO and LaFeO$_3$/rGO sample, which confirms the presence of the elements in the samples. For pure graphene oxide only C and oxygen were present in the sample hence it further confirms the purity of the material. From the LaFeO$_3$/rGO EDS spectra, it is
further confirmed that no elements other than La, Fe, C and O were present hence it shows that the prepared samples were highly pure.

![Figure 6.9 EDS spectra of (a,b) GO and LaFeO$_3$/rGO nanocomposites](image)

6.4.7 High Resolution Transmission Electron Microscopy Studies

Figure 6.10 shows the TEM images and corresponding HRTEM images of the LaFeO$_3$ nanospheres. It was observed for the TEM image that the LaFeO$_3$ sample shows sphere-like morphology with uniform size distribution. From the HRTEM image the interference fringe was clearly observed with d-spacing of 0.393 nm corresponds to the (101) plane. The SAED pattern (inset of Figure 6.10b) clearly indicates the crystalline nature of the LaFeO$_3$. From the image J software it was found that the average diameter of nanosphere was about 45 nm. The size of the particle agrees well with both HRSEM and XRD results.

TEM images of graphene shown in Figure 6.11(a-c), exhibits a crumpled surface and scrolling edges, indicating the successful synthesis of graphene. The HRTEM images of the graphene taken at the edge of the sheet shows that the graphene consists of 3–4 layers (Figure 6.11d). In addition, the
SAED pattern of graphene clearly exhibits bright dots arrangement which demonstrates the feature of graphene (inset Figure 6.11d).

Figure 6.10 TEM and HRTEM images of LaFeO$_3$ nanospheres

Figure 6.11 HRTEM images of GO Nanosheets
Figure 6.12 shows the typical TEM images of LaFeO$_3$/rGO nanocomposites.

![Figure 6.12](image)

**Figure 6.12** HRTEM images of LaFeO$_3$/rGO nanocomposite annealed at N$_2$ atmosphere

From the TEM images, it is clearly seen that the LaFeO$_3$ nanoparticles were decorated on the surface of GO, and the agglomeration of the particles is effectively prevented compared to bare LaFeO$_3$ nanoparticles. It is expected that the well dispersed nanoparticles on the surface of the GO will inhibit the restacking of GO, avoiding the loss of high active surface area in the composite. The corresponding SAED (inset, Figure 6.12d) pattern displays diffraction rings, signifying the polycrystalline nature of the LaFeO$_3$/rGO composite. The HRTEM images (inset, Figure 6.12d) of LaFeO$_3$/rGO composites display interference fringes with d-spacing of 0.393
nm corresponds to (101) planes of the LaFeO$_3$ crystal and also suggest that LaFeO$_3$ nanoparticles are grown on the surface of GO. LaFeO$_3$/rGO exhibits the same interlayer spacing (0.393 nm), corresponds to the (101) crystal plane, indicating that no change occurred in the lattice structure of LaFeO$_3$ after GO was introduced.

6.4.8 Atomic Force Microscopy Studies

Figure 6.13 shows the AFM morphological images of LaFeO$_3$, GO and LaFeO$_3$/rGO nanocomposites. For pure LaFeO$_3$ (Figure 6.13(a,b)) it was observed that the morphology of the sample was composed of fine spherical nanoparticles with uniform size distribution. As shown in the Figure 6.13(c,d) the graphene sheets have wrinkles and folds with an average thickness of 6.7 nm and length of about 3.1 µm indicating that a thin graphene sheet was obtained.

![AFM images](image)

Figure 6.13 AFM images of (a,b) LaFeO$_3$, (c,d) GO and (e,f) LaFeO$_3$/rGO nanocomposites annealed at N$_2$ atmosphere
Figure 6.13(e,f) shows the AFM images of LaFeO₃/rGO nanocomposites annealed at N₂ atmosphere it was observed from the image that the graphene sheets was decorated homogeneously with LaFeO₃ nanoparticles, indicating uniform growth of the LaFeO₃ on the graphene sheet. Hence the AFM results were similar to that of HRSEM and HRTEM results.

6.4.9 Formation Mechanism of LaFeO₃/rGO Nanocomposites

![Schematic representation of the synthesis procedure for LaFeO₃/rGO Nanocomposites](image)

Figure 6.14 Schematic representation of the synthesis procedure for LaFeO₃/rGO Nanocomposites
The synthesis method involves electrostatic interactions between the metal cations and GO. Precipitation of metal precursors was achieved using ammonia solution on GO via a hydrothermal treatment, which can reduce the post calcinations process at high temperature to produce a single-phase LaFeO$_3$/rGO composite. Scheme (Figure 6.14) also illustrates that the metal cations were coordinated with the functional groups of GO to form a mixture of metallic ion/GO, where these metal cations were converted to a cluster of metal hydroxides by adjusting the pH of the mixture using ammonia. Furthermore, the hydrothermal treatment assisted by calcinations can yield crystallite growth of LaFeO$_3$ nanoparticles on rGO.

### 6.4.10 Magnetic Property Studies

![M-H hysteresis loops of LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites at room temperature](image)

The magnetic properties of LaFeO$_3$ and LaFeO$_3$/rGO nanocomposite were studied by magnetic hysteresis at room temperature (300
K) (Figure 6.15). The LaFeO$_3$ nanoparticles showed a typical weak magnetic hysteresis loop at room temperature with the specific saturation magnetization (Ms) of 1.152 emu/g. The LaFeO$_3$/rGO nanocomposite prepared by both N$_2$ and air atmosphere showed a similar magnetic behaviour with a lower specific saturation magnetization (Ms) of 0.419 emu/g which is very low when compared with LaFeO$_3$. This may be due to the incorporation of carbon in the LaFeO$_3$.

### 6.4.11 X-Ray Photoelectron Spectroscopy Studies

X-ray photoelectron spectroscopy (XPS) has been proved to be a useful tool for identifying the oxidation state of elements. Figure 6.16(a,b) shows the wide range survey spectra of GO and LaFeO$_3$/rGO composites. The XPS survey spectrum of GO sample confirms the presence of C and O. The XPS survey spectrum of LaFeO$_3$/rGO exhibits characteristics peaks corresponding to La 3d, Fe 2p, C 1s and O 1s, suggesting the formation of a composite phase.

![Figure 6.16 Wide range survey spectra of (a) GO and (b) LaFeO$_3$/rGO sample](image)

Figure 6.16 Wide range survey spectra of (a) GO and (b) LaFeO$_3$/rGO sample
From the Figure 6.17a it can be seen clearly that GO shows three most prominent deconvoluted components, with one of them assigned to sp²- C 1s (at ~285 eV) and the other two assigned to species of C–O (hydroxyl and epoxy) and C=O (carboxyl) with binding energy of ~287 and ~289 eV respectively (Zhan et al 2011). This clearly shows high degree oxidation of GO.

![Figure 6.17 XPS spectra of GO sample](image)

**Figure 6.17 XPS spectra of GO sample (a) core level of C 1s region (b) core level of O 1s region**

From the Figure 6.18a the peaks of La 3d₅/₂ and La 3d₃/₂ were situated at 834.4 eV and 838.4 eV and at 851.2 eV and 855.4 eV, respectively. The spin-orbit splitting of La 3d level is 16.8 eV and it is similar to the previous report (Zhang et al 2013). In Figure 6.18b, the peaks at 710.6 and 724.4 eV correspond to the binding energies of Fe 2p₃/₂ and 2p₁/₂, respectively (Parida et al 2010). No noticeable shoulder peaks are found in the Fe 2p XPS spectrum, indicating that Fe mainly exhibits +3 oxidation state. The XPS peak of C 1s located at 284.6 eV (Figure 6.18c) is the characteristic of graphitic carbon, which corresponds to the C–C bond. The binding energies of ~285, ~287 and ~289 eV are assigned to C=C, C–O and C=O bonds, respectively. The XPS peak area ratios of the C=O bond to the C–C bond show that most
carbon atoms are sp\(^2\) hybridized, suggesting that most of the oxygen-containing functional groups of graphene in LaFeO\(_3\)-graphene are removed.

Figure 6.18  XPS spectra of LaFeO\(_3\)/rGO sample (a) core level of La 3d region (b) core level of Fe 2p region (c) core level of C 1s region (d) core level of O 1s region

6.4.12  UV-Vis Absorption Spectral Studies

Figure 6.19 shows the UV-Vis absorption spectra of LaFeO\(_3\) and LaFeO\(_3\)/rGO nanocomposites. It was observed from the spectra that the light absorption of LaFeO\(_3\)/rGO in the visible region extensively increased when compared with LaFeO\(_3\). Both the curves exhibit a broad absorption band in the wavelength ranging from 400 to 600 nm, which strongly indicates that both the samples can absorb considerable amounts of visible light, implying
their potential applications as visible light-driven photocatalysts. In addition, after the calculation of the band gap, the values were determined to be 2.52 eV for LaFeO$_3$/rGO and 2.66 eV for LaFeO$_3$. This result indicates that graphene can make the band of LaFeO$_3$ narrow.

![Absorbance spectra of LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites](image)

**Figure 6.19** UV-Visible absorbance spectra of LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites

6.4.13 Photocatalytic Property Studies

The photocatalytic performance of both LaFeO$_3$ and LaFeO$_3$/rGO composites were tested for the degradation of MO in aqueous suspensions under visible light irradiation. Figure 6.20 shows the UV-Vis time dependent absorbance spectra during photocatalytic reaction of MO for LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites after visible light irradiation. Initially we have tried without any photocatalyst, the result shows only 3% of degradation within 180 min visible light radiation. After visible light radiation for 180 min by using LaFeO$_3$ as photocatalyst, the absorption peak intensity at 465 nm which corresponds to MO gets weakened dramatically. Under the same
condition, the photocatalytic activity was enhanced extensively, when LaFeO$_3$ was introduced by graphene. After 180 min, the absorption peak was very low and the intense orange colour of the starting MO solution faded. This suggests that both the LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites were effective catalysts for MO degradation. As shown in Figure 6.20 when using LaFeO$_3$/rGO as photocatalyst under visible light for 180 min, the decolorization rate of the dye reached 97% and for pure LaFeO$_3$ the decolorization rate of the dye reaches only 83%. Hence the photocatalytic efficiency of LaFeO$_3$/rGO was higher than that of the LaFeO$_3$.

![Photocatalytic activity enhancement](image)

**Figure 6.20** UV-Vis time dependent absorption spectra during photocatalytic reaction of MO for LaFeO$_3$ and LaFeO$_3$/rGO nanocomposites. Degradation percentage of MO as the function of irradiation time. Optical photograph showing gradual Color change of MO at different time intervals during photodegradation process.
6.5 CONCLUSION

The LaFeO$_3$/rGO nanocomposites were synthesised by hydrothermal method and their photocatalytic behaviour was investigated. XRD result confirms the formation of LaFeO$_3$, GO and LaFeO$_3$/rGO phase. FT-IR and Raman spectra showed the successful transformation of LaFeO$_3$, GO and LaFeO$_3$/rGO. It was found that optical property of this nanocomposite could be enhanced by the interaction between LaFeO$_3$ and GO compared with the pure LaFeO$_3$. The enhancement of UV-Vis light photocatalytic activity result from the high separation efficiency of photoinduced electron–hole pairs promoted by graphene hybridization and the graphene can accelerate the adsorption of the dye. HRSEM and AFM results suggest the formation of a layer by layer structure of LaFeO$_3$/rGO nanocomposites with dense packing of LaFeO$_3$ nanoparticles between the layers of GO. TEM and HRTEM investigations also suggest that the nanoparticles do not experience agglomeration. It was concluded that the unique structural features of the LaFeO$_3$/rGO nanocomposite, including layer by layer assembly, tight packing and dispersibility of the nanoparticles atop the GO, cause a synergistic effect between LaFeO$_3$ nanoparticles and GO, which significantly improved the photocatalytic performance. The catalytic experimental results indicate that the incorporation of LaFeO$_3$ with GO can significantly enhance the photocatalytic activity when compared with LaFeO$_3$ nanoparticles.