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Photocatalytic Degradation of Malachite Green Dye via An Inner Transition Metal Oxide-Based Nanostructure Fabricated through a Hydrothermal Route †

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Abstract: This experimentation focuses on, an inner transition metal oxide-based nanostructure $LaFeO_3$ which was fabricated by hydrothermal route for photocatalytic degradation of dye under visible light irradiation. The fabricated nanostructure was characterized by various techniques X-ray diffraction (XRD) depicts the crystalline nature and size of the synthesize nanostructure which is 45 nm, Field emission scanning electron microscopy (FE-SEM) which determined the overall morphology of the nanocomposite and energy dispersive X-ray (EDAX) analysis which established the presence of La, O, and Fe in the sample. The photocatalytic activity of the samples was checked for the decolorization of malachite green (MG) dye. It was observed that the nanostructure showed maximum response with more than 80% degradation of MG in 80 min.

Keywords: malachite green dye; photocatalysis; $LaFeO_3$.; perovskite; hydrothermal synthesis

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1. Introduction

The materials having a size dimension in the nano-range exhibit outstanding physical and chemical properties as compared to the bulk material [1,2]. Nanostructured materials have received significant consideration because of their involvement in miscellaneous areas, i.e., drug development, farming, bioengineering, transport, nutrition supplements, devices, space, packing materials, fabric, microchip technology, and cosmetics industries [3–5]. Perovskites having general formula ABO_3 have shown to possess outstanding characteristics because of their unique structure and properties such as electric conduction, insulator, ferroelectric, magnetic, thermochemical, and catalysis. Furthermore, these characteristic properties can be easily manipulated by changing the particular ratio of rare-earth ions A and B in the perovskite oxides [6,7]. The replacement of ions is the finest tactic to boost the efficient characteristics of the nanostructure, which can be exploited for new-generation nanostructure materials [8,9]. ABO_3 type mixed oxide perovskite nanostructures such as $LaMnO_3$, $LaNiO_3$, $PbTiO_3$, and $LaCrO_3$, [10] have been recognized and because of their tremendous photocatalytic activity, they are generally used as a photocatalyst in wastewater remediation applications [11,12]. Release of dangerous manufacturing wastes into the water bodies and air results in critical ecological problems [13]. Henceforth it is compulsory to eradicate these dangerous ingredients before releasing them into the environment. The noxious ingredients produced from colorants can be eradicated via physiochemical tactics like co-precipitation, nano photocatalysis, nano adsorption, nanofiltration, and advanced oxidation processes [12]. A competent technique

like photocatalysis has appeared for the decontamination of wastewater. In the typical procedure, electron-hole pairs accumulated at the valence band and at the conduction band are produced by band-gap energy, responsible for redox reactions with the recalcitrant adsorbed on the exterior of the nanophotocatalyst [13]. The reaction conditions like the pH of the reaction, the quantity of the photocatalyst, substrate concentration, and treatment time nanophotocatalytic performance have also been explored. Photocatalytic tactics are cast-off as a pre-treatment for the conversion of non-biodegradable organic contaminants to biodegradable compounds owning low molecular weight [14]. The linking of semiconductor photocatalysts shows greater photocatalytic capability thus increasing the charge transfer and outspreading the energy range of photoexcitation [15].

This assessment is concentrated on the fabrication and characterization of the $LaFeO_3$ nanostructure fabricated through the hydrothermal route. The surface area and conductivity of $LaFeO_3$ can be enhanced by substituting the Fe metal ions in the ABO_3 lattice. Characterization of the prepared nanostructured material was done by transmission electron microscopy (TEM) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). The photocatalytic performance of the fabricated nanostructure was evaluated by means of the photodegradation of Malachite green dye. Malachite green dye is a dye used as an antifungal in ponds and lakes. It is cast-off in paper manufacturing, and in cloth industry for dyeing silks [16]. It is a water-soluble dye and may be carcinogenic, and can cause chromosome disorders, and skin diseases [19]. The synthesized $LaFeO_3$ nanostructure degraded approximately 82% of the dye in 80 min only.

2. Materials and Methods

The Malachite dye used was purchased from Sigma Aldrich (USA). The photocatalysis tests were performed under visible light. The crystallinity and phase identification purity of the synthesized $LaFeO_3$ were detected by using a diffractometer (XRD, Rigaku Ultima IV, Tokyo, Japan). FTIR spectra were obtained using a spectrophotometer (Nicolet iS50 FTIR Tri-detector). The morphology of the nanostructures was carried out by a Scanning Electron microscope (FESEM) Company Zeiss Gemini SEM 500 with EDS detector and the perovskite nanostructure was determined by Transmission electron microscope (TEM) (JOEL-JSM 6360, Japan).

Synthesis

The $LaFeO_3$ nanostructure was fabricated by the hydrothermal route using lanthanum nitrate and, and ferric nitrate nonahydrate in equimolar amounts as a precursor and then dissolved in 40 mL double distilled water with continuous magnetic stirring fallow by dropwise addition of NaOH to maintain pH. After strong stirring, the mixture was relocated into a Teflon-line stainless autoclave and heated at 200 °C for 14 h [17–21]. The resultant precipitate was filtered, washed with DI water and ethanol, and then dried at 90 °C to get the dark-colored $LaFeO_3$ nanostructure powder. The photocatalytic activity of the $LaFeO_3$ nanostructures in the eradication and decomposition of Malachite dye was assessed at room temperature. For every trial, 30 mg of nanostructures was distributed in 60 mL of the Malachite dye solution.

3. Results and Discussion

3.1. Characterization

Figure 1a XRD depicts the crystalline nature and size of the synthesized nanostructure which is 45 nm calculated by the Debey Sherrer equation, all peaks matched well with JCPDS card no. 00-037-1493. Figure 1b FTIR confirmed the fabrication of a metal oxide-based nanostructure via peaks between 4000-400 cm^{-1}. Figure 1c reveals the cubic morphology of the $LaFeO_3$ nanostructure, where the rough surface of the $LaFeO_3$ nanostructure is clearly visible [22,23]. TEM images depicted in Figure 1d revealed the perovskite assembly of the synthesized nanostructure. EDX spectrum depicted in Figure 1e revealed

the presence of La, O, and Fe elements in the synthesized nanostructure. The Tauc plot depicted in Figure 1f revealed the band gap energy which is 2.61 eV [24].

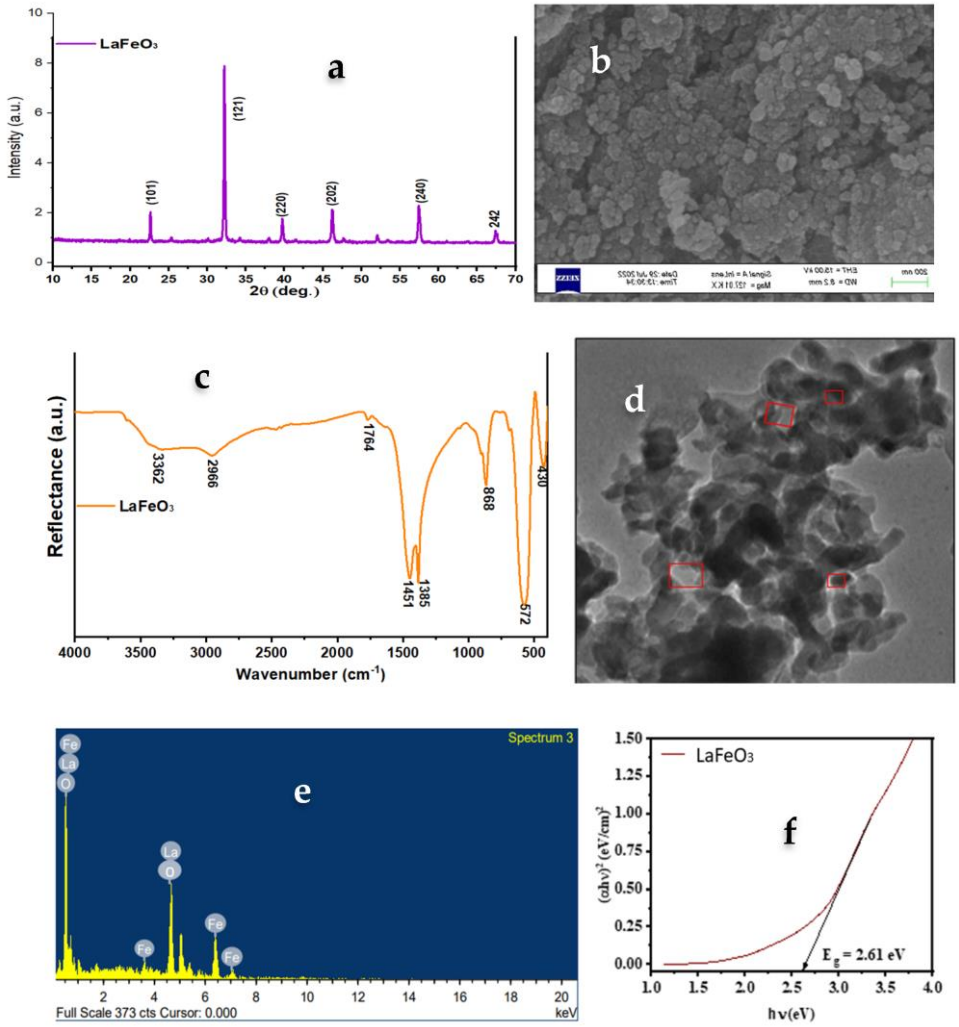


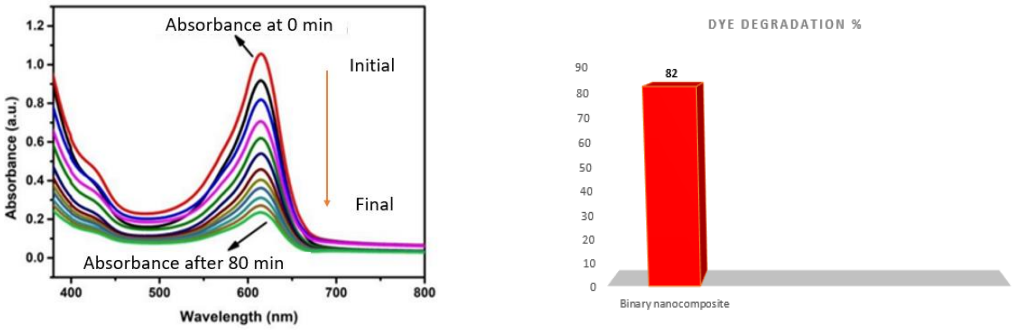
Figure 1. (**a**) XRD spectra (**b**) FTIR spectrum (**c**) SEM images, (**d**) TEM images (**e**) EDX, (**f**) Tauc plot of the synthesized $LaFeO_3$ nanostructure.

3.2. Photocatalytic Activity of $LaFeO_3$ Nanostructures

The degradation percentage of MG was 82% in 80 min as depicted in Figure 2a,b. Due to an increase in reactive site, charge transfer across the interfaces, and efficient absorption of visible light. 30 mg catalyst was dispersed in 60 mL of MG (10 PPM) dye solution and maintained at constant stirring under sunlight. 3 mL solution is removed at intervals of 5 min from the sample for the UV-Vis study. Equation 1 was used to calculate the percentage of malachite green absorbed on the catalyst surface [24,25].

$$\text{Percentage of degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 represents the initial time in absorption and C_t represents the absorption minutes.



(**a**) (**b**)

Figure 2. (**a**) Photodegradation of malachite green dye in aqueous solution under visible light for $LaFeO_3$ (**b**) Bar graph representing dye degradation percentage.

The Photodegradation Mechanism of MG is depicted in Figure 3a. An upsurge in MG adsorption on the $LaFeO_3$ nanostructure surface might have reacted with reactive oxygen species (ROS) in the photocatalysis procedure. When $LaFeO_3$ was treated by visible light irradiated, hole and electron pairs were created on the valence band (VB) and conduction band (CB) of the $LaFeO_3$ photocatalyst (Equation (2)), An electron on the conduction band generates superoxide (Equation (3)). Superoxide reacts with water and generates hydroxyl radical (Equation (4)). In continuation, the hole can also react with the hydroxyl group from water generates •OH radicals (Equation (5)), [26,27]. The hydroxy radicals react with the dye and degrade the dye into CO_2 and H_2O as depicted in Figure 3b. The kinetics of photodegradation was 0.00356 min^{-1}.

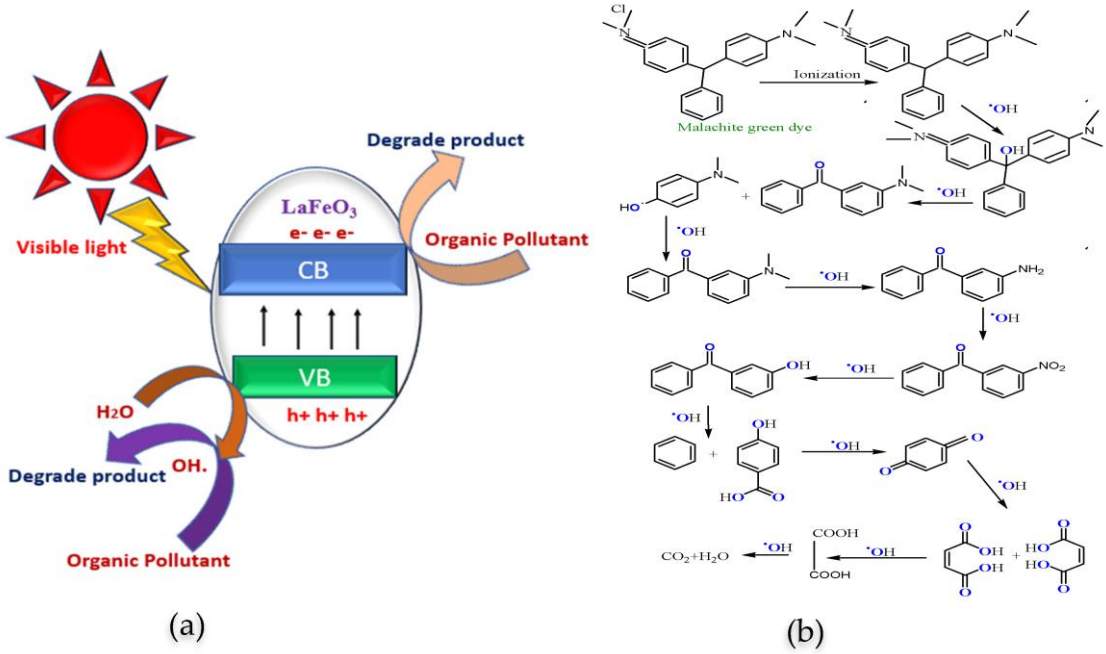


Figure 3. (**a**) Photocatalytic mechanism of synthesized nanocomposite (**b**) Dye degradation steps involves reactive oxygen specie.

$$LaFeO_3 + h\nu \rightarrow LaFeO_3 (e^-_{CB} + h^+_{VB}) \quad (2)$$

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$O_2^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + {}^{-}OH + O_2 \quad (4)$$

$$h^{+}_{VB} + H_2O \rightarrow {}^{\bullet}OH \quad (5)$$

$$\text{Reactive species } ({}^{\bullet}OH, O_2^{\bullet-}) + \text{Dye (organic pollutant)} \rightarrow \text{Degradation products} \quad (6)$$

The degradation percentage of MG is 82% due to an increase in reactive site, charge transfer across the interfaces, and efficient absorption of visible light.

4. Conclusions

Synthesis of $LaFeO_3$ nanostructure has been successfully performed by the Hydrothermal method. The $LaFeO_3$ nanostructure composite has high photocatalytic activity in the removal and degradation (82%) of the dye in 80 min, due to the large surface area, small band gap, and fast charge transference character. $LaFeO_3$ nanostructure, it could be utilized as a nano photocatalyst for wastewater remediation and can be further explored in heterojunction formation.

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