Review

LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} (0 \leq x \leq 1) spherical nanostructures prepared via ultrasonic approach as photocatalysts

Madappa C. Maridevaru\textsuperscript{a}, Sambandam Anandan\textsuperscript{a,*}, Belqasem Aljafari\textsuperscript{b}, Jerry J. Wu\textsuperscript{c}

\textsuperscript{a} Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Trichy 620015, India
\textsuperscript{b} Department of Electrical Engineering, College of Engineering, Najran University, Najran 11001, Saudi Arabia
\textsuperscript{c} Department of Environmental Engineering and Science, Feng Chia University, Taichung 407, Taiwan

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\textbf{A B S T R A C T}

To harvest the photon energy, a sequence of perovskite-type oxides of LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} (0 \leq x \leq 1) nanostructures with distinct ‘Cobalt’ doping at the position of B-site are successfully prepared via a simple ultrasonic approach as photocatalyst. The crystallinity, phase identification, microstructure, and morphology of perovskite nano-composites were analyzed to better understand their physicochemical properties. The catalytic efficiency was assessed using Congo Red (CR) dye by visible light irradiation for 30 min. Applying terephthalic acid as a probe molecule, the formation of hydroxyl radicals during the processes was investigated. The photocatalytic efficacy was measured by varying different Co/Fe stoichiometric molar ratios and noticed the order of sequence is 0.2 > 0.6 > 0.4 > 0.8 > 0.5 > 0 > 1 after 30 min of reaction time. Finally using LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} nanostructures, cycling studies (n = 3) were performed to determine its photostability and reusability. The photocatalytic methodology proposed in this study was discussed extensively.

1. Introduction

Perovskite oxides with general chemical formula ABO\textsubscript{3}, have more potential towards transducers, [1–4] magneto resistance devices, [5,6] and in catalytic reactions because of its chemical stability, crystal structure, electrical, and piezoelectric capabilities. [7–9] Furthermore, the perovskite having corner-shared BO\textsubscript{3} octahedral coordination network, which enables electron transfer, [10,11] and greatly improved partial replacement on A and/or B-sites cations are attributed to better photocatalytic activity. [12–14] In this regard, LaFeO\textsubscript{3} perovskite has received great attention with extraordinary performance, towards inventive applications, including solid oxide fuel cells, [15,16] sensors, [17,18] magnetic materials, [19] and environmental remediation. [20–23] This is due to the adequate bandgap (~2.1 eV) of LaFeO\textsubscript{3}, which plays a major role in catalytic activity and has received much attention for its applicability in the solar energy sensitive characteristic. [24–26] The iron mixed-oxide perovskite (LaFeO\textsubscript{3}) doped with cobalt in B-site (for ex. LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3}) regulates the electronic structure, bandgap, and oxygen vacancy properties, to realize the versatile characteristics and enhanced photocatalytic performance. [27,28] LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} is shown to be suitable for a variety of applications, including water purification, methane oxidation, sodium-ion batteries, and catalyst for hydrogen generation by water splitting and degradation of dye pollutants. [29–31] Azo (-N = N-) dyes (Congo Red, Acid Orange, Methyl red, Tartrazine, Sudan red, etc.) are the most frequently used dyes in textiles and certain other associated industries such as paper, plastic, pharmaceutical, leather, and so on. [32–35] Congo Red (CR) is a sodium salt of the benzidine diazo-1-naphthylamine-4-sulfonic acid [36] is chosen for this study due to its unusual characteristics like hydrophobic, non-biodegradable, anionic nature, and severe environmental concerns. [37,38] Such effluent combines directly with rivers and other nearby water bodies, causing water pollution. The CR dye effluent is highly carcinogenic, it poses a serious threat to aquatic animals and human life. [39] Several physicochemical approaches such as biodegradation, [40] microbial/enzymatic treatment, [41] adsorption, [42] coagulation [43], and flocculation are employed to eliminate CR pollutants. These processes produce huge volumes of sludge, which causes disposal issues. Unfortunately, the conventional techniques described above are ineffective in removing azo dyes. [44,45] Hence, in recent decades, many researchers have extensively focused on advanced oxidation processes (AOPs) as a significant technique for effective decomposition of dangerous toxic chemicals contained in wastewater into less hazardous...
CO2 and water, while also being a less expensive and low-temperature process. [46,47] Semiconductor photocatalysts absorbed sunlight, enable to generate hole (h\textsuperscript{+}) and electron (e\textsuperscript{-}) pairs, which initiate oxidation reactions with strong reactive oxidizing radicals (e.g., OH\textsuperscript{-}) generated in these reactions for conversion of organic contaminants to innocuous products. [48–53] The earlier reported photocatalytic approaches with metal oxides have some drawbacks, which could be overcome by developing a novel photocatalyst for efficient CR dye degradation under visible photon irradiation.

In this context, following a simple ultrasonic technique to synthesize LaCo\(_{1-x}\)Fe\(_x\)O\(_3\) perovskite nanomaterials and investigate their catalytic performance in the presence of visible photons using CR dye as a pollutant. Furthermore, the benefits and drawbacks of the current approach are thoroughly discussed.

2. Experimental section

2.1. Materials and equipment used

All precursor chemicals utilized in the present study were of analytical reagent grade and were utilized as purchased without further additional purification. Lanthanum nitrate hydrate [La(NO\(_3\))\(_3\)·6H\(_2\)O, 99.9 %, CAS no. 10277–43–7], was procured from Alfa Aesar, India. Cobalt nitrate hydrate [Co(NO\(_3\))\(_2\)·6H\(_2\)O, ≥98%, CAS no. 10026–22–9], and Potassium hydroxide [KOH, ≥98%, CAS no. 1310–58–3] purchased from Sigma-Aldrich, India. Iron (III) nitrate nonahydrate [Fe(NO\(_3\))\(_3\)·9H\(_2\)O, ≥98%, CAS no. 7782–61–8] was obtained from Merck Life, India. Congo red (CR) ([Co\(_2\)H\(_2\)N\(_2\)O\(_2\)S\(_2\), product no. 22120, CAS no. 573–58–0), was received from Loba Chemie Pvt. Ltd., Mumbai, India. De-ionized (D.I.) water was utilized for the preparation of an aqueous solution throughout the work. Fabricated a photocatalytic chamber (The Revathis Enterprises, Chennai, Tamil Nadu, India) of dimensions (W × H × L = 47x30 x 32 cm\(^3\)) with cooling fans to maintain a steady temperature within the chamber throughout the experiment.

2.2. LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) perovskites synthesis

The catalyst with the formula LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) (with x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0) was synthesized by a single step ultrasonication process in a typical experiment. Initially, a stoichiometric amount of (0.075 mol; 2.509 g) La(NO\(_3\))\(_3\)·6H\(_2\)O, (0.075 mol; 0.802 g) Fe(NO\(_3\))\(_3\)·9H\(_2\)O (0.075 mol; 1.01 g) was added to 100 mL of distilled water, stirring constantly, and then adding an aqueous KOH solution to the precursor mixed solution until pH value of 12 was attained, stirring and dissolving till the clear monogeneous precipitate was produced, after washing with double distilled water followed by acetone, and dried at 80 \(^\circ\)C. The wide-angle Rigaku D/max-2500 X-ray diffractometer with a Cu-K\textsubscript{α} radiation (λ = 1.54 A\(^\circ\)) source with 40 kV accelerating voltage and an intensity of 200 mA with Ni filtered was utilized to investigate the phase identification and crystalline structure of the LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) samples. The spectra were taken at a 2\(^\circ\)/min scanning speed in the 2-theta degree range from 10\(^\circ\) to 90\(^\circ\). Field emission scanning electron microscopy (FESEM model JEOL, JSM-6700F), high-resolution transmission electron microscopy (HR-TEM model FEI Tecnai G2 F20 microscope piloted at 300 kV), and selected area electron diffraction (SAED) were used to examine the surface morphology and microstructural properties of the synthesized LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) samples. An energy-dispersive analyzed X-ray spectrometer (EDAX, Oxford Inc coupled to FESEM) and elemental color mapping was done to identify the elemental composition. Using Physical Electronics PHI 5600 X-ray photoelectron spectroscopy (XPS) quantification study was performed on the chemical states of the elements survey with monochromatic Al K\textsubscript{α} (photon energy – 1361 eV) excitation source. The optical properties of the as-synthesized material were explored using a UV–vis spectrophotometer (T90 + double beam, PG Instruments, UK) with BaSO\(_4\) as reference material and the photoluminescence spectra of the synthesized samples were obtained by a Shimadzu (RF5301PC) spectrophotometer.

2.4. Photocatalytic experimental setup for Congo red (CR) dye degradation

The degradation of CR dye (\(\lambda_{\text{max}}\approx 498 \text{ nm}\)) was conducted under visible light irradiation at natural pH (8.5) and under the ambient condition to assess the catalytic activity of the synthesized LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) perovskite samples. The photoreactor consists of three Osram Low-voltage halogen lamps without reflector (400 mm; 24V/150 Watts, Nominal luminous flux – 5000 lm, radiation intensity – 80,600 lx), that emit light which is equivalent to natural visible source radiation. In a photoreactor, 100 mL of 3 \times 10\(^{-5}\) mol/L of CR dye solution were taken in a 125 mL borosilicate glass bottle. Around 20 mg of catalyst was added and a chemically inert magnetic stir bar covered with polytetrafluoroethylene (PTFE) was inserted in the aforementioned solution to produce stirring action. The solution was kept for 10 min in the dark to achieve adsorption and desorption equilibrium between catalyst surface and dye molecules. Following this procedure, to reach photocatalytic degradation, the suspension was subject to light illumination for 30 min. At regular sampling intervals, 4 mL of the aqueous suspension from the reactor was sampled and filtered through a 0.45 µm pore size PVDF membrane syringe filter to remove the photocatalyst particles, owing supernatant solution. Following that, a UV–vis spectrophotometer (T90 + Double beam UV–Vis spectrophotometer) was utilized to evaluate the concentration of a supernatant solution by measuring the absorption at its characteristic wavelength (200 nm–800 nm) using 1 cm optical quartz cuvettes with a 4 mL volume. Calculating the changes in the absorbance of the reaction solution revealed the degradation efficiency \(η\), % of CR dye using equation (1).

\[
\text{Dye degradation efficiency (η) = } \left| \frac{A_0 - A_t}{A_0} \right| \times 100\%
\]

where, \(A_0\) and \(A_t\) are the concentration and absorbance of the CR dye solutions before degradation and after degradation treatment, respectively. Moreover, the rate constant (k) of photocatalytic performance was obtained by utilizing the first-order rate equation (2).

\[
-\ln\frac{A_0}{A_t} = kt.
\]

2.5. Analysis of hydroxyl (OH\textsuperscript{•}) radical generation

A simple photoluminescence (PL) approach was used to analyze hydroxyl (OH\textsuperscript{•}) radicals. 20 mg of the photocatalyst was introduced to the 100 mL of 2 \times 10\(^{-3}\) mol/L terephthalic acid in an alkaline solution (Conc. 1 × 10\(^{-3}\) mol/L NaOH). At sampling intervals, 4 mL of aliquots were procured and the catalyst was filtered using a PVDF membrane syringe filter (0.45 µm). The PL analysis was then performed with an excitation wavelength at 315 nm.

3. Results and discussion

Several characterization techniques were utilized to validate the
preparing perovskite-type LaCo$_{1-x}$Fe$_x$O$_3$ nanoparticles. The XRD studies were utilized to identify the phase and crystalline structure of the as-prepared nanomaterials. The XRD pattern (range 10°-90°) of as-prepared LaCo$_{1-x}$Fe$_x$O$_3$ (0 ≤ x ≤ 1) perovskite-type oxides sintered at 800 °C is shown in Fig. 1. The sharpness of the diffraction patterns reveals the prepared samples are highly crystalline, and all of the XRD peaks were so well correlated with the standard JCPDS No.37-1493 data of LaFeO$_3$ and JCPDS No. 48-0123 data of LaCoO$_3$ indicating the sample’s purity. [54,55] The detected XRD peaks for LaCoO$_3$ prepared LaCo$_{1-x}$Fe$_x$O$_3$ composites, as well as homogeneity. The SEM-EDS spectra of other LaCo$_{1-x}$Fe$_x$O$_3$ (x = 0, 0.4, 0.5, 0.6, and 1) are provided in Supporting Information (Fig. S1).

The optical absorption and energy band characteristics of LaCo$_{1-x}$Fe$_x$O$_3$ perovskite samples were investigated using a high-resolution XPS and the results are presented in Fig. 5 (a-e). The survey spectrum shown in Fig. 5a confirmed the presence of La, Fe, Co and O only and no other corresponding elements identified. The survey results are well matched with SEM-EDS analysis and the C 1s peak at 288.5 eV is assigned as a reference peak. Four peaks 835.4 eV-838.1 eV and 852.3 eV-854.9 eV were assigning La 3d$_{5/2}$ and La 3d$_{3/2}$ respectively (Fig. 5b). [61,62] The observed XPS spectra results of La 3d$_{5/2}$ at 835.4 eV and La 3d$_{3/2}$ at 852.3 eV are closely matched with the standard XPS values of La 3d$_{5/2}$ at 836.0 eV and La 3d$_{3/2}$ at 853.0 eV. The 16.9 eV peak gap between La 3d$_{5/2}$ and La 3d$_{3/2}$ implies the presence of La$^{3+}$ valence state in perovskite form. [63]

The Fe 2p peak presented in Fig. 5c can be split into two peaks, Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, with binding energy values of 711.1 eV and 724.9 eV, respectively, corresponding to the Fe$^{3+}$ ion in its oxide structure. [64] The perovskite’s Co 2p spectrum shown in Fig. 5d was fitted by two prominent peaks at 781.1 eV, which is comparable to Co$_2$O$_3$ at 779.2 eV, and 797.8 eV, which were assigned to the existence of Co$^{3+}$ with the basic satellite peak at 787.2 eV. [65] Fig. 5e reports three peaks at 528.9, 530.9 eV, and 533.2 eV that have indexed the lattice, adsorbed, and hydroxyl oxygen, respectively. That 530.9 eV peak was linked to asymmetric and wide O 1 s spectra, confirming the existence of an oxygen (O$^2-$) network in the LaCo$_{2}$Fe$_{0.8}$O$_{3}$ perovskite lattice. [66] The above valuable information from the XPS surveys, confirms the chemical framework of LaCo$_{2}$Fe$_{0.8}$O$_{3}$ perovskite. The optical absorption and energy band characteristics of LaCo$_{1-x}$Fe$_x$O$_3$ nanoparticles may have a significant impact on their catalytic performance. Herein, Fig. 6a displays the diffused reflectance spectra of LaCo$_{1-x}$Fe$_x$O$_3$ (0 ≤ x ≤ 1) perovskites produced at various Cobalt doping stoichiometric ratios. The optical absorption spectra of the samples result from the entire absorption edges that extend beyond 580 nm, indicating that they can respond well in the visible range. As a result, the materials’ characteristics can be investigated utilizing visible photon-driven methodologies (photocatalysis). Using the equation (3), evaluated the optical energy bandgap (E$_{g}$) of the prepared samples:

$$\frac{1}{h\nu} = \frac{1}{E_{g}} + \frac{1}{h\nu}$$

where the absorption coefficient is referred to as ‘α’, photon energy is represented by ‘hν’, the frequency of the stimulated photon, C is the
constant, and $E_{g,\text{bulk}}$ is the sample’s bandgap energy. The m value is based on the kind of transitions in semiconductors. According to theoretical results, for direct transition ($m = 2$) and indirect transition ($m = 1/2$). Plotting ($\alpha h\nu$) against the light energy ($h\nu$) and extending the plotline, as shown in Fig. 6b, provides the semiconductor’s energy bandgap.

The bandgap energies obtained for the LaCo$_x$Fe$_{1-x}$O$_3$ materials ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) which were evaluated to be 1.89, 1.83, 1.94,
to regulate the optical response of LaCo\textsubscript{x} with x = 2.15, 2.08, 1.98 and 2.31 eV, respectively. The sample with Cobalt doping, (x = 0.2) had the lowest bandgap (1.83 eV), whereas the sample with x = 1 had the highest energy bandgap (2.31 eV). These results support future photocatalytic experiments by demonstrating the ability to regulate the optical response of LaCo\textsubscript{x} perovskites by modifying the bandgap. The LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} shows improved photocatalysis performance by synergic effect and narrow bandgap energy allowing more visible light to be absorbed.

The following Mott-Schottky relation is also used to generate an energy level diagram (ELD) for the theoretical evaluation of the relative band edge position of the photocatalysts. Moreover, identifying the conduction band (E\textsubscript{CB}) and valence band (E\textsubscript{VB}), potential edge values of the LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} nanoparticle samples were evaluated approximately (Table 1) by utilizing the following equation (4) and (5):

\[
E_{VB} = X - E_0 + 0.5E_g \tag{4}
\]

\[
E_{CB} = E_{VB} - E_0 \tag{5}
\]

where, E\textsubscript{CB}, E\textsubscript{VB}, E\textsubscript{g}, and X are represented the CB potential edge, VB potential edge, energy bandgap, and absolute electronegativity of the as-synthesized LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} samples, respectively. E\textsubscript{0} stands for free-electron energy on the H\textsubscript{2} scale (4.5 eV vs NHE). The X value of the LaFeO\textsubscript{3} and LaCoO\textsubscript{3} is calculated to be 5.58 eV and 5.64 eV, respectively [67,68] with the reference absolute electronegativities values of La, Fe, Co, and O were 3.1, 4.06, 4.3, and 5.74 eV, respectively as mentioned in ‘Pearson Absolute Electronegativity table’. The VB potential value for the LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} sample (E\textsubscript{VB} = 1.605 eV) was determined to be the lowest in the sequence, with a CB potential of ~0.225 eV leading to a narrow bandgap (1.83 eV) that absorbs optimum visible photons. Photocatalytic activity necessitates the excitation of VB electrons towards the high-energy transition levels in the CB, which resulted in the production of electron-hole pairs. A lower potential of the VB position facilitates this excitation and increases the redox potential of photocatalytic efficacy.

The photocatalytic performance of the LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) perovskites toward photodegradation of aqueous CR dye solution at natural pH (8.5) was monitored by UV – visible absorption spectroscopy under simulated visible photon illumination. Fig. S2 in supporting information depicts the structure and absorption spectra of CR dye. The \( \pi - \pi^* \) transition is assigned to the high energy absorption signal at 343 nm, another low energy peak around 498 nm might be attributed with n- \( \pi^* \) electron transition existent in the nitrogen of an azo chromophore (\( N = N \)) group. The photocatalytic effectiveness at various Cobalt doping rates was determined under optimal circumstances (Fig. 7 (a-b)) using visible photon irradiation for 30 min. The significant catalytic efficacy was observed with Cobalt doping at the B-site when compared with pristine LaFeO\textsubscript{3} perovskite. The photocatalytic efficacy varying with different Co/Fe stoichiometric molar ratios was noticed in the sequence of 0.2 > 0.4 > 0.6 > 0.8 > 0.5 > 0 > 1 after 30 min of reaction time. Among all synthesized samples, LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} perovskite revealed 81 % of photocatalytic efficacy of CR dye degradation after 30 min under the visible photon illumination shown in Fig. 7a. In the absence of a photocatalyst, no significant reduction (only 3.1 % degradation) in CR dye concentration is reported under visible light is presented in Fig. 7b. The first-order kinetic model was employed to estimate the photocatalytic degradation of CR dye after 30 min irradiation on LaCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} nanoparticles (the calculated rate constant values were 0.01118, 0.0461, 0.02308, 0.01642, 0.02516, 0.01706 and 0.00947 min\(^{-1}\), respectively min\(^{-1}\), for x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1 respectively) displayed in Fig. 8(a-b) and Table 2. The LaCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3}...
perovskite nanocomposite sample exhibited the maximum photocatalytic performance with a rate constant of 0.0461 min\(^{-1}\) in 30 min. According to the observations, the rate constant for LaCo\(_{0.2}\)Fe\(_{0.8}\)O\(_3\) is 5-fold more than that of pure LaCoO\(_3\) and LaFeO\(_3\) samples. As compared the catalytic efficacy of as-prepared LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) samples with previously reported CR dye degradation using various nanocatalysts were presented in supporting information Table S1. It is found that as-prepared photocatalyst showed superior catalytic ability towards CR dye (3x10\(^{-5}\) M) degradation in 30 min at natural pH.

Further investigations on the LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) perovskite samples revealed that the degradation of CR dye was dependent on the initial dye concentration in the aqueous solution. Fig. 9a illustrates the variation of CR dye content in solutions as a function of light stimulation duration. Photocatalytic degradation efficacy was investigated using a defined concentration of LaCo\(_{0.2}\)Fe\(_{0.8}\)O\(_3\) perovskite samples (20 mg) with constant adsorption sites, on the variation of initial CR dye concentrations ranging from 2 x10\(^{-5}\) mol/L to 5 x10\(^{-5}\) mol/L at natural pH-8.5 as revealed in Fig. 9a and supporting information Fig. S3. The rate of photodegradation was enhanced initially up to a CR dye concentration

![Fig. 5. XPS spectra of LaCo\(_{0.2}\)Fe\(_{0.8}\)O\(_3\) perovskite sample, (a) survey spectra, (b) La, (c) Fe, (d) Co and (e) O elements in composite.](image1)

![Fig. 6. (a) Absorbance spectra and (b) Tauc plot of synthesized LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) perovskite samples.](image2)

| Catalyst sample | Bandgap (eV) | E\(_{\text{VB}}\) (eV) | E\(_{\text{CB}}\) (eV) |
|-----------------|--------------|---------------------|---------------------|
| LaFeO\(_3\)     | 1.89         | 2.015               | 0.125               |
| LaCo\(_{0.2}\)Fe\(_{0.8}\)O\(_3\) | 1.83         | 1.605               | -0.225              |
| LaCo\(_{0.4}\)Fe\(_{0.6}\)O\(_3\) | 1.94         | 2.095               | 0.195               |
| LaCo\(_{0.5}\)Fe\(_{0.5}\)O\(_3\) | 2.15         | 2.245               | 0.095               |
| LaCo\(_{0.6}\)Fe\(_{0.4}\)O\(_3\) | 2.08         | 2.165               | 0.085               |
| LaCo\(_{0.8}\)Fe\(_{0.2}\)O\(_3\) | 1.98         | 1.68                | -0.3                |
| LaCoO\(_3\)     | 2.31         | 2.295               | -0.015              |

![Table 1: Bandgap energies with potential edge positions of VB and CB of LaCo\(_{x}\)Fe\(_{1-x}\)O\(_3\) samples in different Cobalt rates from 0 to 1.](image3)
of 3 x10^{-5} \text{ mol/L}, afterwards the rate diminished as the CR dye concentration was increased further. At optimum CR dye concentrations, a significant number of catalyst molecules are accessible to adsorb the majority of the molecules in suspension, whereas, at higher CR dye concentrations, a significant number of CR dye molecules compete for active sites (screening effect), which leads to diminishing the degradation rate.

The effects of adjusting the dose of LaCo_{0.2}Fe_{0.8}O_3 perovskite samples on CR decolorization proficiency are shown in Fig. 9b and supporting information Fig. S3. The initial CR dye concentration was fixed (3 x10^{-5} \text{ M}) at natural pH (8.5), while adding LaCo_{0.2}Fe_{0.8}O_3 samples of about 10, 20, 30, and 40 mg/100 mL, the photocatalytic rate altered. In the absence of LaCo_{0.2}Fe_{0.8}O_3, the CR dye remains unaffected after 30 min in the visible photon. The maximal photocatalytic efficacy of CR dye was achieved by increasing the dose of LaCo_{0.2}Fe_{0.8}O_3. Under visible photons, 81% of color pollutants degraded after 30 min with LaCo_{0.2}Fe_{0.8}O_3 loading of 20 mg/100 mL, may be ascribed to the abundance of surface-active sites of photocatalyst for degradation. However, further elevating the LaCo_{0.2}Fe_{0.8}O_3 content did not result in a considerable improvement in degradation rate, due to the increased particles’ opacity and light scattering.

Finally, the catalytic activity mechanism of LaCo_{0.2}Fe_{0.8}O_3 nanoparticles was studied to be coherent with the different analytical results. Based on the following facts, we can postulate that the contributing factors on catalytic activity might be associated with crystallite size, energy bandgap, and reactive species. Initially, the small crystallite size of the material shows the fast photon-generated charge carriers migrate from the bulk to the active surface, enhancing the catalytic efficacy on the surface before recombination. The bandgaps of the Cobalt doped LaFeO_3 samples were varied and the positions of the VB and CB edges were regulated to accelerate CR dye degradation.

Generally, the possible mechanism of photodegradation of dyes pollutants on catalyst surface is caused by either photocatalytic oxidation or photosensitization of dye displayed in Fig. 10. The dye is activated in the photosensitization mechanism by capturing visible photons, while the most efficient degradation is achieved by photocatalytic oxidation in which the reactive oxygen species are generated on the surface of the catalyst.

### Table 2

| Sl. no | Sample           | Rate Constant (min^{-1}) | R^2 value |
|-------|------------------|--------------------------|-----------|
| 1     | Light only       | 0.00093                  | 0.973     |
| 2     | Dark condition   | 0.00576                  | 0.987     |
| 3     | LaFeO_3          | 0.01118                  | 0.981     |
| 4     | LaCo_{0.2}Fe_{0.8}O_3 | 0.04610             | 0.961     |
| 5     | LaCo_{0.4}Fe_{0.6}O_3 | 0.02516             | 0.975     |
| 6     | LaCo_{0.5}Fe_{0.5}O_3 | 0.01642             | 0.944     |
| 7     | LaCo_{0.6}Fe_{0.4}O_3 | 0.03016             | 0.910     |
| 8     | LaCo_{0.8}Fe_{0.2}O_3 | 0.01706             | 0.988     |
| 9     | LaCoO_3         | 0.00947                  | 0.933     |
source photons and then transferring electrons to the catalyst’s conduction band, which combines with the oxygen in the surface to generate a superoxide oxidant to induce the degradation as presented in equation (6–9) [72]:

\[ \text{CR} + h\nu \rightarrow \text{CR}^* \]  
\[ \text{CR}^* + \text{LaCo}_{0.2}\text{Fe}_{0.8}\text{O}_3 \rightarrow \text{CR}^* + \text{LaCo}_{0.2}\text{Fe}_{0.8}\text{O}_3(e_{\text{CB}}) \]  
\[ \text{LaCo}_{0.2}\text{Fe}_{0.8}\text{O}_3(e_{\text{CB}}) + O_2 \rightarrow O_2^- \]  

Moreover, in the instance of photocatalytic degradation, electron-hole charge pairs produced on the surface of LaCo_{0.2}Fe_{0.8}O_3 catalyst combine with water and oxygen molecule to produce hydroxyl (OH\(^\bullet\)) and superoxide (O\(_2\)\(^\bullet\)) radicals respectively as shown in equation (10)–(13). The oxidation process is considered to be carried out by photon-generated OH\(^\bullet\) radicals. The azo chromophore group of the dye is initially degraded by these extremely reactive oxidants. [73,74] The photoluminescence approach, which used terephthalic acid (TA) is reacted with OH\(^\bullet\) radical to produce 2-hydroxyterephthalic acid (HTA) which exhibits strong fluorescence and validate the origin of the OH\(^\bullet\) radical. The PL emission spectra of TA in a NaOH solution with a LaCo_{0.2}Fe_{0.8}O_3 catalyst material during visible photon stimulation are displayed in Fig. 11.

\[ \text{LaCo}_{0.2}\text{Fe}_{0.8}\text{O}_3 + h\nu \rightarrow e_{\text{CB}} + e_{\text{VB}} \]  
\[ e_{\text{CB}} + O_2 \rightarrow O_2^- \]  
\[ O_2^- + H_2O \rightarrow HO_2^• + OH^- \]  
\[ HO_2^- + H_2O \rightarrow HO_2 + OH^- \]  

The reusability of the perovskite catalyst in photocatalysis is essential because it reduces the cost expenses of dye pollutant treatment. After every single reaction, the insoluble LaCo_{x}Fe_{1-x}O_3 catalyst was centrifuged, extensively washed with deionized water to eliminate the adsorbed dye moieties, and dried before being employed in further photocatalytic reactions. To accomplish this, three repeated cycles of photocatalytic CR dye degradation were carried out, employing the same catalyst with a fresh dye solution. The catalytic efficiency was reduced by a very less percentage (4%) throughout each cycle, as illustrated in Fig. 12a. The XRD findings of reused sample in Fig. 12b further demonstrate that the manufactured catalyst would not degrade itself and can be easily recycled for extended uses.

4. Conclusions

In conclusion, Cobalt doped perovskite-type oxides LaFeO_3 nanocomposites with varying doping concentrations were successfully manufactured via a single-step ultrasonic approach. The existence of the doped ‘Cobalt’ metals was confirmed by XRD measurements and EDS spectra. XPS survey was used to identify the chemical oxidation states of the elements in the photocatalyst. Under photocatalytic conditions, Cobalt doped catalysts lead to better CR dye degradation efficacy than LaFeO_3. The electronic band structure of a material can be altered by doping with Cobalt on B-site, as is widely known. When exposed to incident radiation, a narrower bandgap of doped catalyst displayed considerable changes in the valence and conduction band positions and provided facile electron accessibility, resulting in a greater synergistic.
effect and improved catalytic activity. The developed LaCo$_{0.2}$Fe$_{0.8}$O$_3$ catalyst displayed high photocatalytic activity for CR dye, accelerating >81% dye degradation and exhibiting a first-order rate constant of 0.0461 min$^{-1}$ upon visible photon illumination for 30 min. This study shows a facile approach to tailoring the essential features of ferrite-based perovskite catalysts for visible range photocatalysis.

CRediT authorship contribution statement

Madappa C. Maridevaru: Conceptualization, Data curation, Writing. Sambandam Anandan: Conceptualization, Data curation, Supervision, Writing – review & editing. Belqasem Aljafari: Software, Writing. Jerry J. Wu: Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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