Investigations on the enhanced dye degradation activity of heterogeneous BiFeO$_3$–GdFeO$_3$ nanocomposite photocatalyst

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ABSTRACT

Perovskite types of nanocomposites of BiFeO$_3$–GdFeO$_3$ (BFO-GFO) has been synthesized using sol-gel route for the first time. The nanocomposite powders were characterized by powder X-Ray diffraction (PXRD) to confirm the existence of mixed crystallographic phases. EDX analysis on nanocomposites estimates the composition of individual element present in BFO-GFO matrix. The induced strain upon loading GdFeO$_3$ (GFO) in BiFeO$_3$ (BFO) matrix has been computed with the aid of Williamson–Hall (W–H) plot. Surface morphologies of nanocomposite powders has been studied using Field Emission Scanning Electron Microscope (FESEM) images. The observed changes in the band gap energies of nanocomposite powders due to the inclusion of GFO has been ascertained from the tauc plots. PL emission of BFO upon loading GFO found to have detected in the IR region due to defect level transition. Finally, the methylene blue dye (MB) degradation characteristics of BFO, GFO and the nanocomposite powders of BFO-GFO have also been studied. The overall results obtained has been discussed in detail.

1. Introduction

Photocatalysis reactions have been extensively used for wastewater treatment [1,2]. The photocatalytic oxidation techniques were found to be best method to solve the environmental water pollution issues and energy crisis problems [3,4]. Wide band gap semiconductors like TiO$_2$, titanates, etc., were found to show high photocatalytic activity to the breakdown of organic compounds only within UV regime [5,6] and it has better stability, low cost, and non-toxicity. To improve the utilization efficiency of sunlight radiation and also to enhance the photocatalytic activity, fresh visible-light-driven photocatalysts with high photocatalytic activity and stability has to be designed [7,8,9,10,11]. Through a variety of reports exist in the literature on visible light photocatalysis [12,13,14,15,16,17,18,19,20,21,22,23], certain materials are more responsive to both UV and visible light. Among them, BiFeO$_3$ (BFO) is a well-known and an important semiconductor photocatalyst because of its huge response to solar radiation, band gap and high stability [24,25,26,27]. With these unique properties, BiFeO$_3$ (BFO) is identified not only as a visible light active photocatalyst, but also a potential material in solar and fuel cell applications. However, photocatalytic activity of BiFeO$_3$ (BFO) is still restricted due to the rapid recombination of electron and holes charge carriers and the conduction band (CB) electrons cannot be efficiently caught fully by O$_2$ to produce a lower surface area and to yield superoxide radicals. It is not very easy for a photocatalyst, based on a single metal oxide semiconductor to satisfy all needs such as stability, chemical inertness and reduced-recombination rate. Therefore, Photocatalyst based on combination of two semiconductors have been developed to increase photocatalytic character. In particular, Heterogeneous photocatalyst with wide band gap and high electric conductance semiconductor could provide a larger surface area and has shown improved dye degradation performance [28]. BiFeO$_3$ based heterogeneous photocatalyst including BiFeO$_3$/g-C$_3$N$_4$, BiFeO$_3$/CuO, BiFeO$_3$/WO$_3$, BiFeO$_3$/Pt [29,30,31,32,33] substantiates the significances of photocatalytic activity of BiFeO$_3$ based compounds. For example, BiFeO$_3$/ZnFe$_2$O$_4$nanostructures exhibit excellent photocatalytic activity for degradation of methylene blue which has been ascribed for the improved visible-light absorption, charge carrier separation and migration [36]. Above all BiFeO$_3$ heterojunction

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photocatalyst systems could show better photocatalytic performance for the photo-degradation of organic dye in aqueous medium, but its ability is shielded due to the rapid charge recombination. Researchers have modified the band energy positions of BiFeO3 by the inclusion of high bandgap semiconductor catalysts to reduce the time of recombination of electron-hole pairs and thereby increasing surface area towards enhancing its photocatalytic activity. In particular, rare earth perovskite oxides with wide bandgap and visible light active semiconductor catalysts could provide a larger surface area and has shown improved photocatalytic cavity. Especially, GdFeO3 (GFO) is a kind of typical rare-earth perovskite oxide, with a steady crystal structure and possess distinct characteristics of optical absorption and photocatalytic activity. It is visible light active semiconductor with a narrow band gap (2.3 ev) [35, 36, 57]. Due to its low density, high stability, non-toxicity, chemical inertness and largescale productivity, it has drawn wide attention to searches for using in various applications such as photoelectric devices, photovoltaic solar cell and photocatalysis [38,39]. Further, its high localized conductivity, low recombination rate and high specific surface area could also increase its overall photocatalytic efficiency in the event of loading with BiFeO3. It is also worth noting that GdFeO3 has suitable band edges that could well match with BiFeO3 band edges to form a direct solid-state Z scheme photocatalytic system, where the photon-generated electrons in conduction band of BiFeO3 will exhibit strong reducibility and the holes in valence band of GdFeO3 will present strong oxidizability. Hence, the combination of two visible light active semiconductors can become an efficient heterogeneous type of photocatalyst with improved visible light harvesting property and in turn can exhibit improved photocatalytic activity with greater stability. With this intention an attempt is made to develop a distinct and sustainable visible light induced BiFeO3/GdFeO3 heterojunction nanomaterial. To the best of our survey there are no much reports on the photocatalytic degradation of methylene blue dye using BiFeO3/GdFeO3 heterojunction photocatalyst.

2. Experimental

All the used chemicals were of analytical grade (AR) and used as received without further purification. The precursors were Bismuth Nitrate Pentahydrate (Merck- 99 % Purity), Iron Nitrate Nano hydrate (Merck -98% Purity), Conc. HNO3 (Merck- 69%), Tartaric acid (Merck – 99%), Gadolinium Nitrate Hexa hydrate (Sigma Aldrich – 99%), Ethylene glycol (Merck – 99%).

2.1. Synthesis of BiFeO3 nanoparticles

BiFeO3 nanoparticles have been synthesized by Sol-Gel method through the literature reviews [40,41]. In a typical synthesis process, 3mmol of Bismuth Nitrate Pentahydrate & 3 mmol of Iron Nitrate Nano hydrate dissolved in 50ml of Distilled water. 3ml of Conc. HNO3 & 3 mmol of Tartaric acid were added along with above solution and stirred gently at 115 °C till it turns into Brownish solid solution. The obtained solution was enabled for drying at the temperature of 150 °C to get brownish dry powders. Upon drying the brown powders were calcined in furnace at 500 °C for 2 h to get phase pure BiFeO3 Nanopowders.

2.2. Synthesis of GdFeO3 nanoparticles

GdFeO3 nanoparticles were synthesized through glycol-assisted sol–gel technique [30]. 15 mmol of Gadolinium Nitrate Hexa hydrate were mixed with in 40 mL of Ethylene glycol to get a transparent solu-

2.3. Synthesis of BiFeO3-GdFeO3 Nanocomposites

BiFeO3-GdFeO3 nanocomposite has been prepared from Sol-Gel synthesis in accordance with previous literature [38]. Initially, 3mmol of Bi(NO3)3.5H2O, 3 mmol of Fe(NO3)3.9H2O and 10 mg of GdFeO3 were added in 50ml of Distilled water. 3ml of Conc. HNO3 and 3mmol of Tartaric acid were then mixed to the above solution. Then the solution was heated at 115 °C with continuously stirring, till it changes into reddish brown solid solution. Subsequently, the solid solution was permitted for drying process at 150 °C to get dry powders. After drying, the reddish-brown powders were calcined at 500 °C for 2 h to get BiFeO3-GdFeO3 nanocomposite powders.

2.4. Photocatalytic test on BiFeO3- GdFeO3 nanocomposites

Photocatalytic activity of the BiFeO3-GdFeO3 nanocomposite was investigated by the degradation of methylene blue (MB) in water under natural sunlight radiation. BiFeO3 and GdFeO3 were used as the photocatalytic reference to find the performance of the BiFeO3-GdFeO3 composite system. In each experiment, 10mg of photocatalyst was added to 10 mL of methylene blue (MB) solution at the concentration rate 10 mg/L. The dye and sample suspension were stirred in dark for 120 min so as to ensure the adsorption/desorption equilibrium. Then the solution was kept under natural sunlight. For every 3 hours interval, about 1.0 mL of degraded dye was sampled and it was separated from the aqueous solution by the way of centrifugation at 6000 rpm for 2 min. The concentration of each degraded solution was monitored.

2.5. Characterization techniques used for BiFeO3-GdFeO3 nanocomposites

Crystal structural analysis of BiFeO3-GdFeO3 photocatalysts was done using a ‘XPERT PANalytical’ make powder X-ray diffractometer (PXRD) in the 20 range 10°-60° with a scan rate of 2°/min. Field emission scanning electron microscope (FESEM) images were recorded using S-3400N Hitachi microscope to study the morphologies of poly-crystalline samples. The elemental compositions of the individual constituents Bi, Gd, Fe etc., have been found from Energy Dispersive X-ray analysis (EDX) analyzer. Electronic spectra of BiFeO3, GdFeO3 and BiFeO3-GdFeO3 have been recorded from JASCO V-670 spectrophotometer in the wavelength regime 200–800 nm. Fourier transform infrared spectroscopy (FTIR) spectra was recorded from KBr pellet method using Shimadzu IR Affinity -1 spectrophotometer in the frequency range400–4000 cm−1. Dye degradation properties of the BiFeO3-GdFeO3 photocatalyst at regular intervals of time was analyzed with the aid of LAB INDIA double beam UV-Vis spectrophotometer (Mode no: U2900) in the wavelength range 200–800nm. The path length was fixed as 10 mm for all experimental trials.

3. Results and discussion

3.1. Powder XRD studies on BiFeO3- GdFeO3 nanocomposites

Fig. 1 shows the powder XRD patterns of the BiFeO3, GdFeO3 and theBiFeO3-GdFeO3 nanocomposites BiFeO3 shows indexed diffraction peaks at 2θ = 32.1° and 2θ = 23.1° corresponding to a R3c space group of rhombohedral phase (JCPDS no. 72-2112) and it indicates the well crystallized BiFeO3 phase produced from sol-gel method [42,43]. No other impurity phases were observed along with BiFeO3 phase. Well broadened peaks of BiFeO3 typically shows the nanoparticles are in nano dimension. Similarly, in case of GdFeO3, the indexed diffraction peaks at 2θ = 23.2°, 26.09°, 32.2°, 33.2°, 33.8° & 34.38° match well with the orthorhombic structure having Pbnm space group. It is also in good agreement with the standard JCPDS card no.00-047-0007 and other earlier reports [44,45]. All other peaks obtained for GdFeO3 have reflected only the orthorhombic signals and no other satellite peaks were found.
In case of BiFeO₃ - GdFeO₃ composites, the BiFeO₃ diffraction pattern continued to be present but in broadened mode with low intensities due to the union of orthorhombic GdFeO₃ crystallites and it has also modulated the sizes of the BiFeO₃ nanoparticles and it is evidenced from the well-defined XRD peaks of BiFeO₃.

The average particle size of BiFeO₃ and GdFeO₃ calculated from Scherer formula were established to be ~24 nm and 11 nm respectively in an isolated phase, whereas in composite phase, the average size crystallites of BFO & GFO dispersed in the size range 14-35 nm.

Upon compositing with GdFeO₃, the doublet diffraction peak of BiFeO₃ around 2θ = 32° and 2θ = 23° found to have merged and it has confirmed that GdFeO₃ particles have homogenously got mixed along with BiFeO₃ powders. Further all the peaks of BiFeO₃ have a shifted towards lower 2θ values and it provides an additional clue for the formation of nanocomposite of BiFeO₃ - GdFeO₃. Similar kind of signature was observed for ZnFe₂O₄/BiFeO₃ heterojunction. Furthermore, no other impurity peaks were appeared other than BiFeO₃ and GdFeO₃ and it indicates that GdFeO₃ has been successfully loaded on the BiFeO₃ particles without destroying its own crystal structure. The overall results confirmed that the heterogeneous BiFeO₃-GdFeO₃ photocatalyst could only be composed of rhombohedral BiFeO₃ and orthorhombic structure of GdFeO₃.

In order to analysis the crystalline strain upon loading GdFeO₃ photocatalyst, Williamson–Hall (W–H) analysis [38] was carried out for BiFeO₃, GdFeO₃ and BiFeO₃ - GdFeO₃ nanocomposite samples. The induced strain and observed changes in crystallite sizes have been estimated using the formulae.

\[ \beta_{hl} = \left[ (\beta_{hl})^2_{\text{measured}} - (\beta_{hl})^2_{\text{monocrystal}} \right]^{\frac{1}{2}} \]

\[ D = \frac{K\lambda}{\beta_{hl} \cos \theta} \]

\[ \epsilon = \frac{\beta_{hl}}{4 \tan \theta} \]

\[ \beta_{hl} = \frac{K\lambda}{D \cos \theta} + 4\epsilon \tan \theta \]

\[ \beta_{hl} \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta \]

where;

- \( D \) - is the crystallite size.
- \( K \) - is the shape factor (0.94).
- \( \lambda \) - is the wavelength of Cu Kα radiation.
- \( \theta \) - is the Bragg angle.
- \( \beta_{hl} \) - is the Full width at half maximum & \( \epsilon \) - represents the Crystalline Strain.

The observed variation in the crystalline strain and average crystallite sizes for BiFeO₃, GdFeO₃ and BiFeO₃ - GdFeO₃ from W–H plots and are shown in Fig. 2. The value of ‘c’ and ‘p’ for each sample is also listed in Table 1. The strain modulation of BiFeO₃ - GdFeO₃ nanocomposite particles due to GFO inclusion has considerably influenced its crystallite sizes.

### 3.2. FESEM analysis on BiFeO₃ - GdFeO₃ nanocomposites

The surface morphologies of the BiFeO₃ and GdFeO₃ in BiFeO₃ - GdFeO₃ nanocomposite have been analysed using a scanning electron microscope. The Field Emission Scanning Electron Microscope (FESEM) micrographs of the BiFeO₃ - GdFeO₃ nanocomposites shown in Fig. 3(a). The white granular particles (clearly visible in between BiFeO₃) represented the GdFeO₃ particles and the quasi-spherical shaped sheet shows the presence of BiFeO₃ in the nanohybrid structure. The presence of hybrid phases in the same field of view confirmed the successful synthesis of nanohybrids of BiFeO₃ - GdFeO₃ from sol-gel route. The white granules of GdFeO₃ nanoparticles are found to be well scattered on the surface as well as on the edges of the BiFeO₃. The distribution of the GdFeO₃ nanoparticles was more homogeneous on the BiFeO₃ spherical sheets. However, agglomeration of the GdFeO₃ nanoparticles occurred during attachment onto the BiFeO₃ quasi-spherical shaped sheet. The agglomerated clumps of GdFeO₃ nanoparticles have irregular shapes and the agglomerate ratio increased with GdFeO₃ loading. Fig. 3(b) shows the Energy Dispersive X-ray analysis (EDX) data indicating the composition of element present in the heterogeneous photocatalyst and it gives an additional confirmation to the presence of GdFeO₃ in the nanohybrid of BiFeO₃ - GdFeO₃ system.

In the case of BiFeO₃ nanohybrid loaded with ZnFe₂O₄ using co-precipitation synthesis [46], it was found that BiFeO₃ exists as spherical particles and ZnFe₂O₄ was noticed as nanoparticles. However, a strong interfacial coupling was observed between ZnFe₂O₄ and BiFeO₃. As similar kind of distinct feature in the morphology has been witnessed for BiFeO₃ and GdFeO₃. The present formation of heterojunction would also

### Table 1

| S. No | Name of the Photocatalyst | Crystallite Size (nm) | Strain |
|-------|--------------------------|----------------------|--------|
| 1     | BiFeO₃                   | ~24 nm               | 6.07 E-3 |
| 2     | GdFeO₃                   | ~11 nm               | 2.94 E-3 |
| 3     | BiFeO₃ - GdFeO₃          | ~14-35 nm            | 2.29 E-3 |
have an appreciable figure of interfacial coupling. Therefore, there shall be ample chances for the facial migration of charge carriers (electrons and holes) in BiFeO₃ - GdFeO₃ based photocatalyst.

3.3. UV-Vis-NIR studies on BiFeO₃ - GdFeO₃ nanocomposites

Optical absorption properties on the synthesised samples of BFO-GFO was characterized by UV-Vis-NIR Spectra and it is shown in Fig. 4(a). GdFeO₃ mainly exhibits absorption in the UV wavelength range and its unique absorption edge is around ~390 nm. On the other hand, the optical absorption of BiFeO₃ lies at 500 nm. For BiFeO₃ - GdFeO₃ composites, they present significantly widen absorption area even beyond 530 nm and obviously makes the absorbance of the composites shifting towards longer wavelength side. This may perhaps due to the formation
of tight chemical bonded surfaces between BiFeO₃ and GdFeO₃. A fair broadening of absorption area upon addition of GdFeO₃ towards visible light region is quite similar to the ideology of D. Moitra et al. [47] in Graphene–BFO composites. Therein, it was pointed out that the change in absorption area upon loading a catalyst with BiFeO₃ is a key indicator for deciding the nature of chemical bonding. Therefore, the improvement in chemical bonding between BFO and GFO nanoparticles could be correlated from the absorption spectrum of the composite samples.

The energy band gaps of the BiFeO₃, GdFeO₃ and BiFeO₃–GdFeO₃ samples were calculated using Kubelka-Munk function [48]. The calculated band gap values are 2.0 eV (BFO), 2.3 eV (GFO) and 1.8 eV (composite) and it is shown in Fig. 4(b). Thus, the introduction of GdFeO₃ on BiFeO₃ shows its ability to effectively narrow down the band gap of BiFeO₃–GdFeO₃ composite which is due to the interaction and synergism between BiFeO₃ and GdFeO₃. The decrease in the band gap energy for BiFeO₃–GdFeO₃ may be due to the fact that GdFeO₃ addition would possibly be decreasing electronic correlation energy with oxygen vacancies introduced by the valence state of Fe³⁺ ions. It is noteworthy to mention here that such significantly enhanced visible light absorption spectrum and lowering of band gap would be helpful for improving the photocatalytic performance.

3.4. Vibrational structure analysis on BiFeO₃–GdFeO₃ nanocomposites

FTIR patterns of BiFeO₃, GdFeO₃ and BiFeO₃–GdFeO₃ photocatalysts are shown in Fig. 5. The spectrum of BiFeO₃ indicates a two IR absorption peaks at ca. 455 and 520 cm⁻¹ corresponding to the overlapping Fe–O stretching and bending vibrations. It is also found as the characteristic absorption of FeO₆ octahedra of the perovskite structure [49]. A weak peak at ~711 cm⁻¹ for BiFeO₃ is assigned to the water absorption from the environment and it is also highlighted in the earlier report [50]. This peak has been found less pronounced in BiFeO₃–GdFeO₃ composite. This would confirm that the hydroscopic property of the BFO-GFO nanocomposite sample is partially lower than the pure gadolinium ferrite.
molecules upon loading with BFO.

The medium IR absorptions in the range 3100–3600 cm\(^{-1}\) and the band at \(\sim 1620\) cm\(^{-1}\) may be ascribed to \(\nu(\text{OH})\) and \(\delta(\text{H}_2\text{O})\) of water molecules absorbed on the photocatalyst surface. In case of BiFeO\(_3\)-GdFeO\(_3\) nanocomposite, a new peak observed at \(\sim 536\) cm\(^{-1}\) is due to the vibration of a Gd–O stretching vibration\(^{[51]}\) and a peak at \(\sim 495\) cm\(^{-1}\) has been attributed to the stretching vibrations of Gd-O-Gd in addition to the vibrations of BiFeO\(_3\). The vibrational spectrum contains both the metal oxide vibrations of Gadolinium ferrite and Octahedral environment (FeO\(_6\)) of bismuth. The vibrational spectrum of the BFO-GFO composite corroborates with the results obtained from both power XRD and SEM images.

3.5. Photoluminescence (PL) studies on BFO – GFO nanocomposites

Room temperature PL spectra has been recorded for BFO, GFO and the composite powders of BFO-GFO by dispersing the particles in acetone and it is shown in Fig. 6. PL spectrum of BiFeO\(_3\) (excited at \(\lambda = 483\) nm) consists of two major emissions at 450 nm and 485 nm and three other feeble emissions could also be detected at 660, 728 and 795 nm. The
emission peaks at 450 and 485 nm are related to the near band emission characteristics of BFO. The other weak signals arose due to defect level emissions. The origin of defects may be from oxygen vacancies in the crystal structure and surface area changes in the crystallites. In respect of GdFeO$_3$, the near band emissions occur at 362 and 398 nm. The defect induced emissions have also been detected at 497 and 726 nm. The blend of BFO and GFO nanocomposite powders has been excited at 398 nm. Apart from interband transitions, a strong emission peak towards the higher wavelength side at 726 nm (Red shift) and a weak shift towards the UV regime at 363 nm was also observed from the spectrum. Similar kind of observation was also witnessed in Gadolinium doped BFO [52]. It has been noticed that the inclusion of gadolinium ferrite in the BFO material has considerably enhanced the PL emission intensities especially at the higher wavelength of 726 nm and also the interband transition at 398 nm. This can also be ascertained from the PL emission of pure GFO material.

The increase in PL intensities in BFO-GFO composite both for the near band transition and defect induced non-radiative transition might have occurred due to these possible reasons (i) passivation of oxygen vacancies upon loading GdFeO$_3$(ii) substantial increase number of trapped electrons giving rise to additional electron made available in the heterojunction (BFO-GFO) interface. This will enhance the space charge separation regime and electrons from CB of GdFeO$_3$ to cause more junction layer diffusion. Similarly, holes diffuses from VB of BFO reaches the heterojunction. This results in the increase in PL intensities of BFO-GFO composite over the individual moieties consequent to the introduction of defect levels in the composite phase.

### 3.6. Photocatalytic dye degradation activity of BiFeO$_3$–GdFeO$_3$ nanocomposites

The photo dye degradation efficiency of methylene blue (MB) dye for BiFeO$_3$, GdFeO$_3$ and BiFeO$_3$–GdFeO$_3$ composites as a function of wavelength (nm) are summarized in Figs. 7(a), 7(b) & 7(c). Methylene blue was scarcely degraded by pure GdFeO$_3$ after 9 hr which showed its limited photocatalytic activity on MB under visible light. The low photo-degradation efficiency of GdFeO$_3$ was confirmed due to its high band gap potential, UV light active absorption area and poor photoelectric conversion. In case of BiFeO$_3$, it can degrade upto 76% of MB after 9 hours of irradiation. The extraordinary MB photodegradation efficiency of 98% was observed for the BiFeO$_3$–GdFeO$_3$ composite after 9 hr of irradiation. Enhanced photocatalytic efficiency of the BiFeO$_3$–GdFeO$_3$ composite may be due to the formation of heterojunction, which could encourage photogenerated electron–hole pairs and thus causes for the enhanced photocatalytic activity. Another important reason for high photodegradation efficiency is due to its low band gap tuning and visible light response. However, the efficiency strongly depend only on the content of the two components in the composite and higher specific area surface would also absorb more Methylene blue dye on the exterior of its particles. Hence it facilitates for the higher photodegradation of MB dye. In order to study the reaction kinetics of Methylene blue degradation, the pseudo-first-order equation according to Langmuir–Hinselwood model [53] has been evaluated and it can be expressed by the equation, where $C_0$ and $C_t$ are the concentrations of MB (mg L$^{-1}$) at different irradiation time of $t$ and $t$ respectively. $k'$ is the pseudo-first-order rate constant of photodegradation (min$^{-1}$) of methylene blue (MB). From Fig. 7 (d), the linear fitting curves of $\ln(C_t/C_0)$ versus irradiation time ($t$) also confirmed the better correlation to pseudo-first-order reaction kinetics for BFO–GFO photocatalyst over the virgin ones. The first order kinetic constant value has been estimated for nanocomposite and virgin samples. The values of $R^2$ have been tabulated in Table 2. Photocatalytic degradation efficiencies have also been calculated both for the parent and nanocomposite particles using Eq. (7).

\[
\text{Efficiency, } \eta(\%) = \frac{(C_0 - C_t)}{C_0} \times 100
\]  

The variation in the efficiencies for BFO, GFO and BFO-GFO composite are is shown in Fig.7(e) and a comparative analysis on the dye degradation efficiencies of few heterogeneous photocatalyst with BFO-GFO has also been tabulated in Table 3. The stability of BiFeO$_3$–GdFeO$_3$ samples has been subjected to investigation for a consecutive trail run of 3 cycles @ 9 hours (h)/cycle to a total of 27 hours. The composite sample was confirmed to be more stable and it was found that the stability remains unchanged even at the 3rd run.

The photocatalyst recovered after every cycle, with help of centrifugation from the aqueous medium has been dried in oven for 4 hours (h). Then the recovered nanocomposite samples can be reused again for the photo degradation of Methylene blue solution under natural sunlight for another 9 hour (h) run. This has been tested for 3 cycles. The absorbance values were found to remain unchanged in all observed cycles. The graph indicating reusability of composites is shown in Fig. 7(f).

### 3.7. Proposed mechanism of photocatalysis in BiFeO$_3$–GdFeO$_3$ nanocomposites

The photocatalytic dye degradation mechanism can be defined using three main steps:

1. Photon absorption over the surface of the photocatalyst;
2. The generation of photo-generated electron-hole pairs and
The dye adsorption photochemical reactions over the surface of the photocatalyst.

A schematic mechanism of the photocatalytic dye degradation of methylene blue using BiFeO₃–GdFeO₃ nanocomposite is explained in Fig. 8. The electron and hole generation in the conduction band (CB) and valence band (VB) were totally depend upon band edge positions of the virgin BiFeO₃ and GdFeO₃. The valance band and conduction band positions for BiFeO₃ and GdFeO₃ were calculated using the Mullikan electronegativity method [54] as per the following steps.

\[ E_{VB} = X + 0.5E_g - 4.5 (E_c) \]  
\[ E_{CB} = E_{VB} - E_g \]  

where, \( E_{VB} \) and \( E_{CB} \) are the valence and conduction band edge potential (w.r.t Normal Hydrogen Electrode (NHE)).

\( X \) is the electronegativity of the semiconductor.

\( E_g \) is the energy of free electron on hydrogen scale (4.5 eV) and.

\( E_c \) is the band gap of the photocatalyst (BiFeO₃ ~1.5 eV and GdFeO₃ ~ 2.4 eV).

It has been computed that the conduction band (CB) and valence band (VB) potentials of the BiFeO₃ are 0.3 eV and 2.3 eV and for the GdFeO₃ semiconductor they are 0.5 eV and 2.8 eV, respectively. The reasonable improvement in the photocatalytic properties for BiFeO₃ –GdFeO₃ nanocomposites can be ascribed to the following three main factors;

Firstly, in the as-prepared BiFeO₃ –GdFeO₃ heterostructures, the BiFeO₃ surfaces are not completely covered by GdFeO₃, resulting both of them being highly available for the photo absorption and encouraging the formation of depletion layers on the surfaces of both semiconductors when exposed to sunlight. Therefore, BiFeO₃ and as well as GdFeO₃ are sensitive for light reaction on methylene blue dye molecules.

Secondly, the synthesis of well-distributed heterogeneous photocatalyst could be an efficient way to increase the photocatalytic activity. As such in our work, well-distributed GdFeO₃ has been successfully synthesized from sol-gel route without any other impurity phases. The average particle size of composite powders appears to have been synthesized from sol-gel route without any other impurity phases. The average particle size of composite powders appears to have been synthesized from sol-gel route without any other impurity phases.

Thus, the separated electrons and holes charge carriers at the junction region would initiate the degradation of dye reactants on the photocatalyst surface, and leads to the effective photocatalytic activity of BiFeO₃–GdFeO₃ nanocomposites.

4. Conclusion

Nanocomposite powders of BiFeO₃–GdFeO₃ has been successfully synthesized from sol-gel route without any other impurity phases. The average particle size of composite powders appears to have been increased upon the inclusion of GdFeO₃ in the BiFeO₃ matrix and it was found to be in the range of 14–35 nm, whereas the parent phases of BiFeO₃ and GdFeO₃ powders show average crystallite sizes between ~10–24 nm. FESEM studies showed that BiFeO₃ exists in quasi-spherical structured sheets and GdFeO₃ particles appear as the white granular ones. Williamson-Hall strain analysis on nanocomposite powders reveals

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4. Conclusion

Nanocomposite powders of BiFeO₃–GdFeO₃ has been successfully synthesized from sol-gel route without any other impurity phases. The average particle size of composite powders appears to have been increased upon the inclusion of GdFeO₃ in the BiFeO₃ matrix and it was found to be in the range of 14–35 nm, whereas the parent phases of BiFeO₃ and GdFeO₃ powders show average crystallite sizes between ~10–24 nm. FESEM studies showed that BiFeO₃ exists in quasi-spherical structured sheets and GdFeO₃ particles appear as the white granular ones. Williamson-Hall strain analysis on nanocomposite powders reveals
the fact that there exists an appreciable change in the crystalline strain upon loading GdFeO3 with BiFeO3 and it fairly agrees with the other results for the possible inclusion of GdFeO3 in the BiFeO3 matrix. UV-Vis-NIR studies on BiFeO3–GdFeO3 suggest that band gap tuning found to have occurred due to the addition GdFeO3 in the nanocomposite phase. The band gap energies of BiFeO3–GdFeO3 was found as 1.8 eV, whereas the BiFeO3and GdFeO3 figured 2.0 eV and 2.3 eV respectively. The reduction in the band gap energy values of BiFeO3–GdFeO3 nanocomposites favours for the improved light harvesting property of the nanocomposite phase. FTIR vibrational structure analysis confirm the existence of nanocomposite phase and the vibrations of both moieties do appear in the final compound. Photoluminescence measurements on BFO-GFO composite has shown that there is a reasonable improvement in PL emission at the higher wavelength size upon loading GFO in BFO and it is attributed to the defect – band transmission. However, it has not affected its photocatalytic activity in visible portions. MB dye degradation activity of BiFeO3–GdFeO3 nanocomposites shows that the synthesized powder is capable of degrading 98% of dye molecules and converts them as a reusable water, whereas the parent compounds namely BiFeO3 and GdFeO3 found to be capable of degrading 76% and 42% of MB dye. The reusable capacity of the photocatalyst after dye degradation with nanocomposites powders have been ascertained for a consecutive trail of 3 runs. The absorbance values remain invariant. Thus, the obtained nanocomposite powders of BFO-GFO could be a potential candidate for photocatalytic dye degradation applications.

Author contribution statement
Yathavan Subramanian: Performed the experiments; Contributed reagents, materials, analysis tools or data.
Venkatapathy Ramasamy: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
R J Karthikeyan, Gokul Raj Srinivasan, Durairajan Arulmozhi: Contributed reagents, materials, analysis tools or data.
Ramesh Kumar Gubendaran: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
Mohan Sriramalu: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Declaration
There is no competing interest or financial conflict of interest.

Additional information
No additional information is available for this paper.

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Declarations

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