



Investigations on the enhanced dye degradation activity of heterogeneous BiFeO₃–GdFeO₃ nanocomposite photocatalyst



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ABSTRACT

Perovskite types of nanocomposites of BiFeO₃–GdFeO₃ (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 GdFeO₃(GFO) in BiFeO₃ (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 TiO₂, 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, BiFeO₃ (BFO) is a well-familiar 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, BiFeO₃ (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 BiFeO₃ (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 O₂ 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]. BiFeO₃ based heterogeneous photocatalyst including BiFeO₃/g-C₃N₄, BiFeO₃/CuO, BiFeO₃/WO₃, BiFeO₃/Pt [29, 30, 31, 32, 33] substantiates the significances of photocatalytic activity of BiFeO₃ based compounds. For example, BiFeO₃/ZnFe₂O₄ 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 BiFeO₃ 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 slendared 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, 37]. Due to its low density, high stability, non-toxicity, chemical inertness and largescale productivity, it has drawn wide attention to researches 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 matches with BiFeO₃ band edges to form a direct solid-state Z scheme photocatalytic system, where the photo-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 Penta hydrate (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 Penta hydrate & 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 solution. Then, 15 mmol of Ferric Nitrate Nona hydrate [Fe (NO₃)₃·9H₂O] was added into the above solution. After stirring continuously for 4 h along with heating at 110 °C, a brownish red colloidal mixture was obtained. The sol was dried at 120 °C for 8 h and the obtained GdFeO₃based xerogel was precalcined at 450 °C for 0.5 h to remove NO₃ and organic compounds. The remaining powders were heated in furnace at 800 °C for 4 h so as to obtain pure Nanopowders of GdFeO₃.

2.3. Synthesis of BiFeO₃-GdFeO₃Nanocomposites

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-GdFeO₃nanocomposite 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 theBiFeO₃-GdFeO₃ composite system. In each experiment, 10mg of photocatalyst was added to10 mL of methylene blue (MB) solution at the concentration rate10 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 2θ 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 polycrystalline 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 trails.

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 BiFeO₃phase. 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.00-047-0067 and other earlier reports [44,45]. All other peaks obtained for GdFeO₃have reflected only the orthorhombic signals and no other satellite peaks were found.

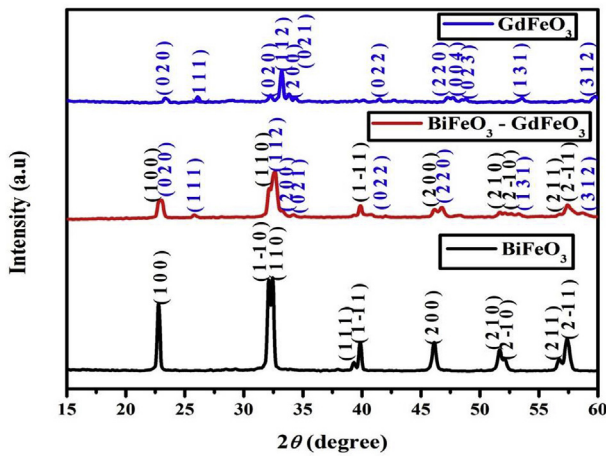


Fig. 1. Powder XRD patterns of BiFeO₃, GdFeO₃ and nanocomposites of BiFeO₃-GdFeO₃.

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 $2\theta = 32^\circ$ and $2\theta = 23^\circ$ found to have merged and it has confirmed that GdFeO₃ particles have homogeneously 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 obtained 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.

$$\beta_{hkl} = [(\beta_{hkl})^2_{\text{measured}} - (\beta_{hkl})^2_{\text{instrumental}}]^{\frac{1}{2}} \quad (1)$$

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (2)$$

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan \theta} \quad (3)$$

$$\beta_{hkl} = \frac{K\lambda}{D \cos \theta} + 4\varepsilon \tan \theta \quad (4)$$

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (5)$$

where;

D - is the crystallite size.

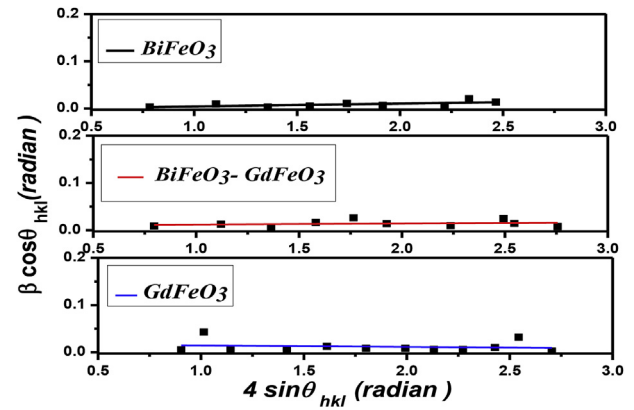


Fig. 2. W-H Plots of BiFeO₃, GdFeO₃ and BFO-GFO nanocomposite powders.

K - is the shape factor (0.94).

λ - is the wavelength of CuK α radiation.

θ - is the Bragg angle

β_{hkl} - is the Full width at half maximum &

ε - 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 ' ε ' and ' β ' 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) represent 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 coprecipitation synthesis [46], it was found that BiFeO₃ exists as spherical particles and ZnFe₂O₄ was noticed as nanoplates. 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

Crystalline strain and crystallite sizes for BFO, GFO and BFO - GFO.

S. No	Name of the Photocatalyst	Crystallite Size (nm)	Strain
1	BiFeO ₃	~24 nm	6.07 E-3
2	GdFeO ₃	~11 nm	2.94 E-3
3	BiFeO ₃ -GdFeO ₃	~14–35 nm	2.29 E-3

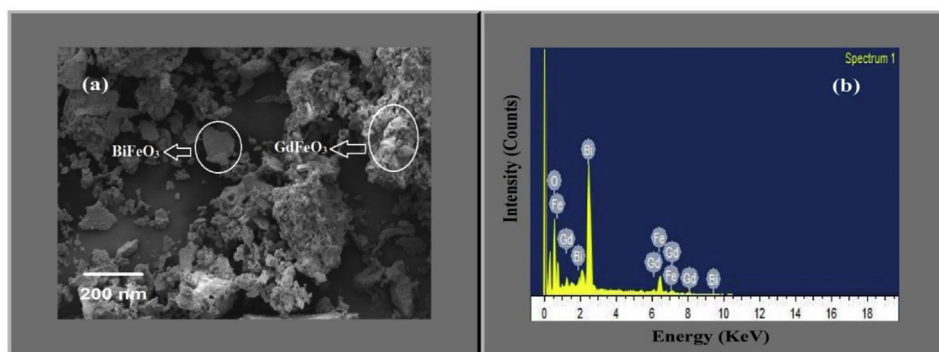


Fig. 3. (a) Dispersion of BFO and GFO nanoparticles in BFO-GFO nanocomposites (b) EDAX mapping of BFO-GFO nanocomposite powders.

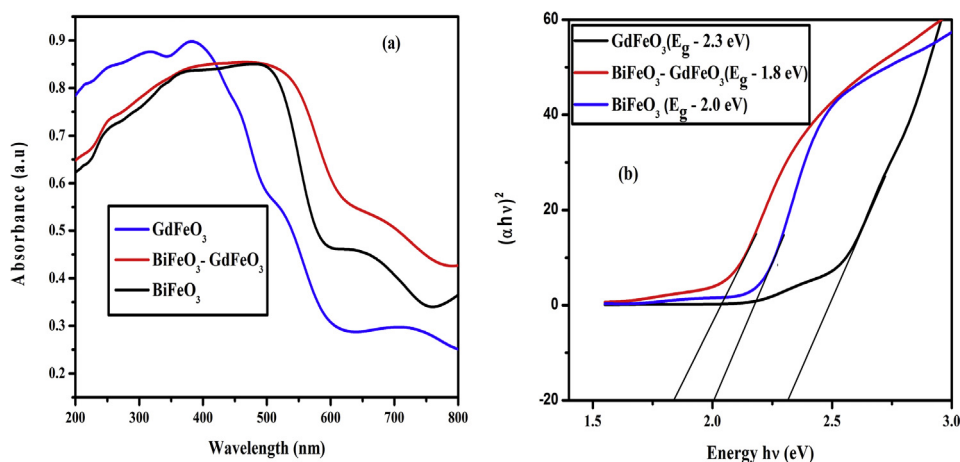


Fig. 4. (a) UV-Vis-NIR spectra of BiFeO₃, GdFeO₃ and BFO-GFO nanocomposite (b) Tauc plots representing the E_g values of BiFeO₃, GdFeO₃ and BFO-GFO nanocomposites.

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 widened 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

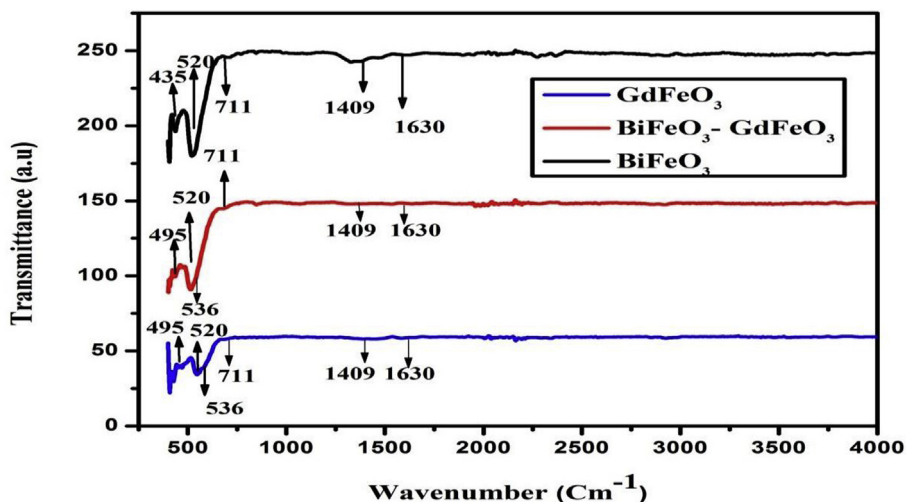


Fig. 5. FTIR spectra of BiFeO₃, GdFeO₃ and BiFeO₃-GdFeO₃ nanocomposite powders.

of tight chemical bonded surfaces between BiFeO_3 and GdFeO_3 . A fair broadening of absorption area upon addition of GdFeO_3 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 BiFeO_3 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 BiFeO_3 , GdFeO_3 and BiFeO_3 - GdFeO_3 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 GdFeO_3 on BiFeO_3 shows its ability to effectively narrow down the band gap of BiFeO_3 - GdFeO_3 composite which is due to the interaction and synergism between BiFeO_3 and GdFeO_3 . The decrease in the band gap energy for BiFeO_3 - GdFeO_3 may be due to the fact that GdFeO_3 addition would possibly be decreasing electronic correlation energy with oxygen

vacancies introduced by the valence state of Fe^{3+} 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 BiFeO_3 - GdFeO_3 nanocomposites

FTIR patterns of BiFeO_3 , GdFeO_3 and BiFeO_3 - GdFeO_3 photocatalysts are shown in Fig. 5. The spectrum of BiFeO_3 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 FeO_6 octahedra of the perovskite structure [49]. A weak peak at $\sim 711\text{ cm}^{-1}$ for BiFeO_3 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 BiFeO_3 - GdFeO_3 composite. This would confirm that the hydroscopic property of the BFO-GFO nanocomposite sample is partially lower than the pure gadolinium ferrite

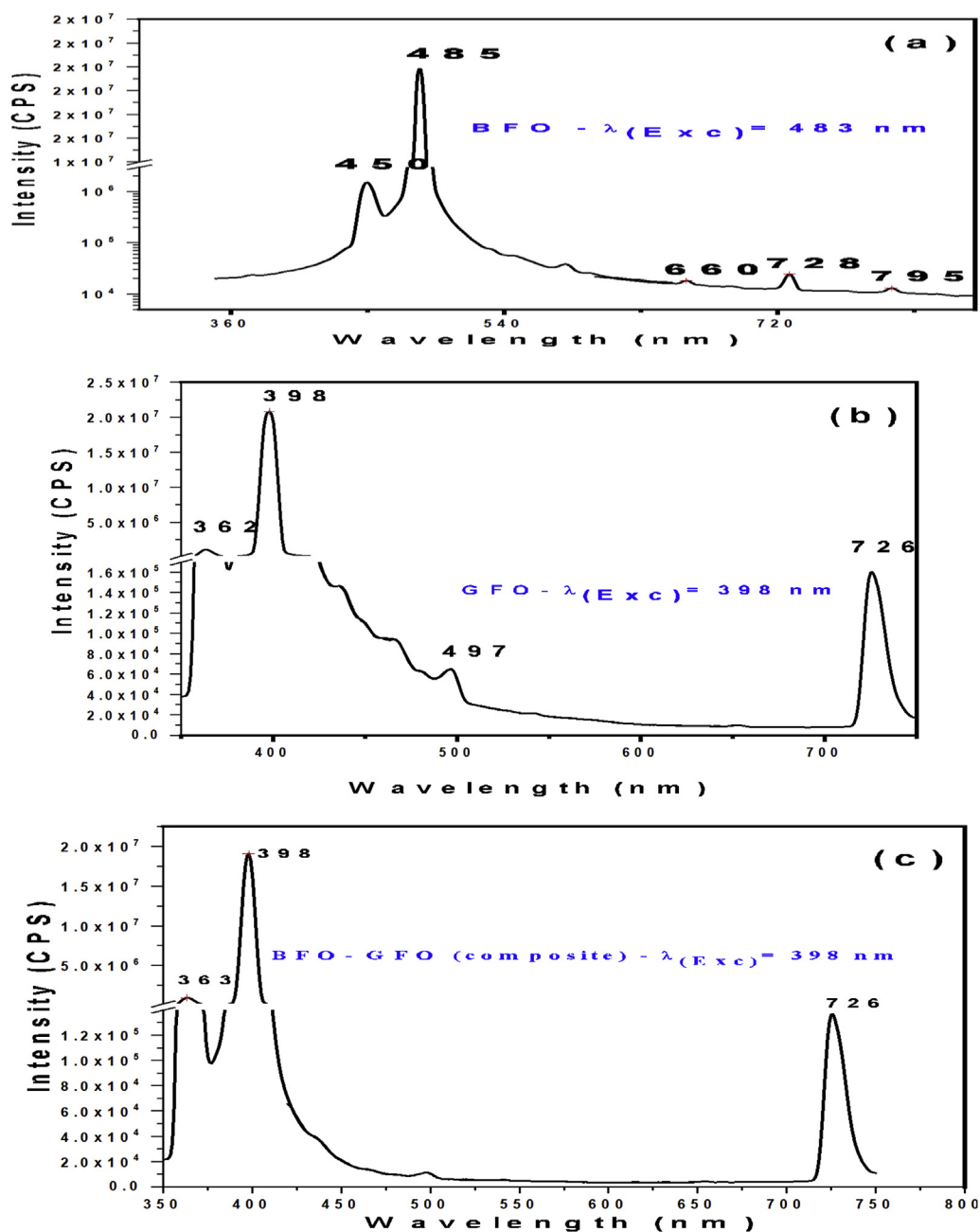


Fig. 6. PL emission spectra of (a) BiFeO_3 , (b) GdFeO_3 and (c) BiFeO_3 - GdFeO_3 nanocomposites.

molecules upon loading with BFO.

The medium IR absorptions in the range $3100\text{--}3600\text{ cm}^{-1}$ and the band at $\sim 1620\text{ cm}^{-1}$ 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 $\text{BiFeO}_3\text{-GdFeO}_3$ nanocomposite, a new peak observed at $\sim 536\text{ cm}^{-1}$ is due to the vibration of a Gd-O stretching vibration [51] and a peak at $\sim 495\text{ cm}^{-1}$ 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 $\lambda = 483\text{ nm}$) 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

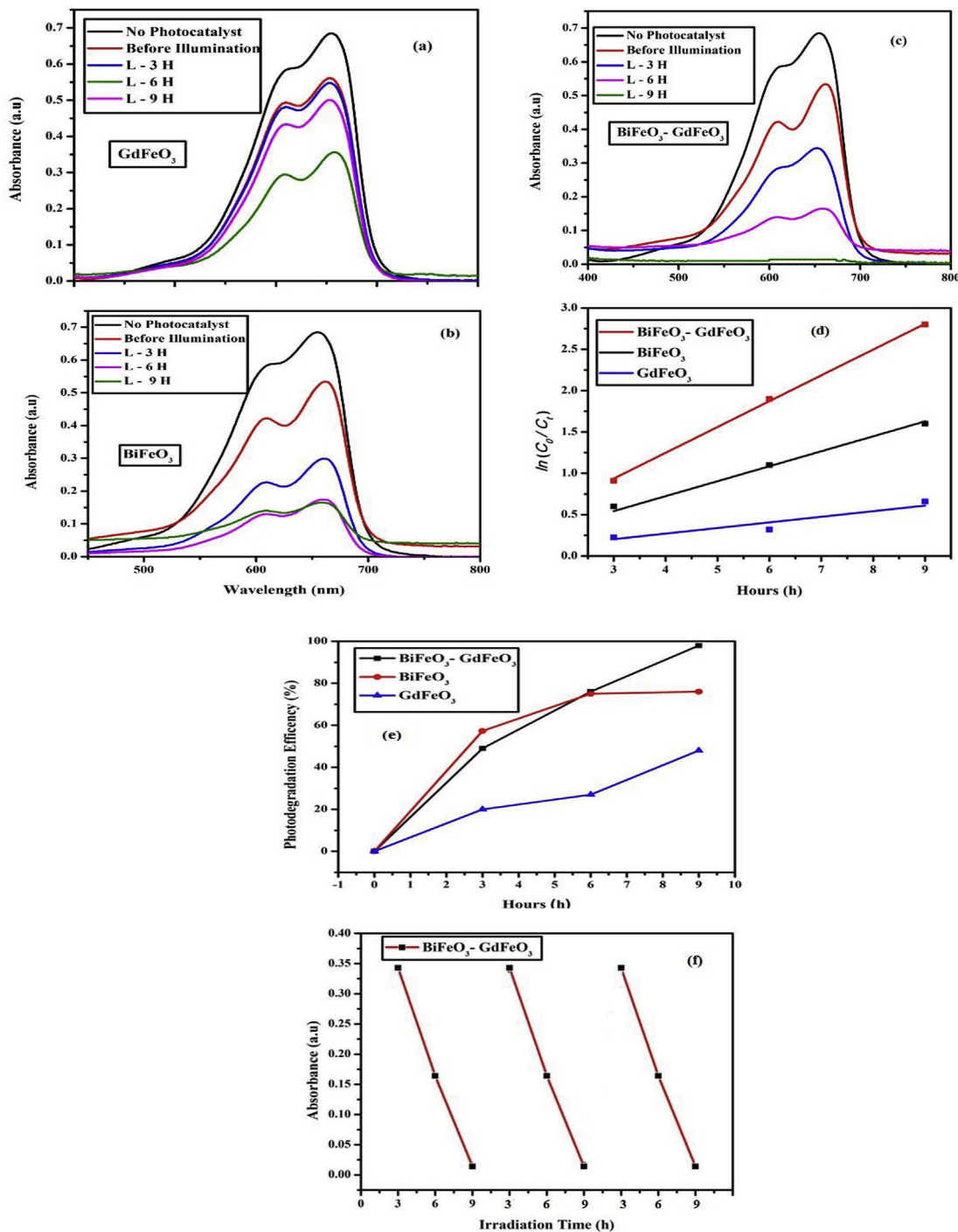


Fig. 7. (a) Wavelength Vs MB dye absorbance for (a) GdFeO_3 , (b) BiFeO_3 suspensions (c) Wavelength Vs MB dye absorbance of $\text{BiFeO}_3\text{-GdFeO}_3$ suspension (d) Exposure time Vs $\ln(C_0/C_t)$ for BFO, GFO and nanocomposites of BFO-GFO (e) Exposure time Vs Photo degradation efficiencies BFO, GFO and BFO-GFOnanocomposites (f) Reusability studies on Methylene blue dye absorbance of nanocomposite of BFO-GFO for every 3 hours interval.

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 photodegradation 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 surface area would also adsorb 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–Hinshelwood model [53] has been evaluated and it can be expressed by the equation,

$$\ln \left(\frac{C_0}{C_t} \right) = kt \quad (6)$$

Table 2

Comparison of rate constants for various photocatalysts with BFO – GFO and their corresponding goodness of fit values.

Estimated values of first order kinetic constants for BFO, GFO and BFO - GFO solution with methylene blue				
S.NO	Photocatalyst	Slope K (min ⁻¹)	Standard Error	R ² Value
1.	BFO	0.18095	0.00412	0.99948
2.	GFO	0.06771	0.00644	0.97338
3.	BFO -GFO	0.31214	0.00246	0.99981

Table 3

Comparative analysis on the dye degradation efficiencies of few heterogeneous photocatalysts.

S. No	Name of Heterogeneous Catalyst	Degradation Efficiency (%)	Reaction condition	Dye used	Time (Hour)
1	SiO_2 – WO_3 [56]	37%	Halogen lamp (72 W, 1520 lm) under visible light at room temperature	Methylene Blue (MB)	3
2	BiFeO_3 /MOF nanocomposite [57]	48%	Visible light irradiation (Xe lamp, 300 W) in a catalytic reactor at 20 °C	Methylene Blue (MB)	3
3	CuO – BiVO_4 [58]	40%	Visible-light irradiation (18-watt fluorescent light), Room temperature	Methylene Blue (MB)	3
4	BiFeO_3 /GdFeO ₃ (Present Work)	56%	Natural sunlight and at atmospheric temperature/condition	Methylene Blue (MB)	3

where C_0 and C_t are the concentrations of MB (mg L⁻¹) at different irradiation time of 0 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 $\ln (C_0/C_t)$ 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).

$$\text{Efficiency, } \eta(\%) = \frac{(C_0 - C_t)}{C_0} * 100 \quad (7)$$

The variation in the efficiencies for BFO, GFO and BFO-GFO composite are 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 each 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

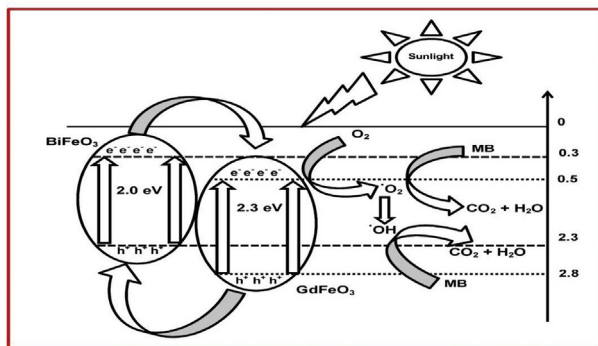


Fig. 8. Z-scheme representation of BFO-GFO nanocomposites.

(3) 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 valence band and conduction band positions for BiFeO₃ and GdFeO₃ were calculated using the Mullikan electronegativity method [54] as per the following steps.

$$E_{VB} = X + 0.5E_g - 4.5 (E_e) \quad (8)$$

$$E_{CB} = E_{VB} - E_g \quad (9)$$

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

E_g 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;

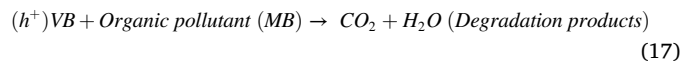
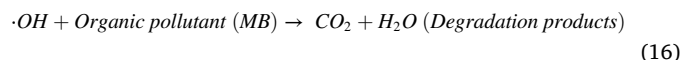
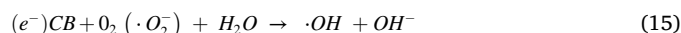
Firstly, in the as-prepared BiFeO₃–GdFeO₃ heterostructures, the BiFeO₃ surfaces are not completely covered by GdFeO₃, resulting both of them being highly available for the photo absorption and encouraging the formation of depletion layers on the surfaces of both semiconductors when exposed to sunlight. 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 are decorated perfectly onto the BiFeO₃ nanoparticles surface through managing pH = 6.0 so as to keep better electrostatic force of attraction between BiFeO₃ and GdFeO₃ semiconductors. The BiFeO₃ nanoparticles can act as a base for the growth of GdFeO₃ nanorods, and avoids the agglomeration of GdFeO₃. The smaller GdFeO₃ on the BiFeO₃ nanoparticles have more exposure and paves way for perfect photon absorption sites to activate and react with dye molecules. Thus, lot of excitations will propagate to the nanocomposite surface, resulting in increased electron extractions from the CB of BiFeO₃ nanoparticles. More electron excitations makes the BFO-GFO nanocomposites sensitive to methylene blue dye for the increased response under the visible portion of light.

Thirdly, due to the strong electronic diffusion between BiFeO₃ and GdFeO₃, a distinct semiconductor junction was formed. Transportation of charge carriers are remarkably enhanced in the hetero-junction, resulting in a quick response. So, BiFeO₃–GdFeO₃ nanocomposites are better

sensitive to methylene blue and have extraordinary properties.

Further, the band gap gets tuned due to the loading GdFeO₃ in BiFeO₃. Since CB of GdFeO₃ are formed above the conduction band in BFO, by increasing the conduction band edge position, it has lead to the reduction of band gap. The electron–hole pair generation inside the conduction band (CB) and valence band (VB) helps to breakdown the organic dye molecules into water molecules (H₂O) and carbon dioxide (CO₂) as by-products under visible light irradiation. The improved photocatalytic activity of BiFeO₃–GdFeO₃ is due to the widening of visible light absorption area and improved redox reactions over the photocatalyst surface. The photo-excited BFO-GFO guides the generation of electron–hole pair charge carriers. According to the energy band edge mechanism diagram in Fig. 8, the photo-generated electron in the conduction band of the BiFeO₃ will move towards GdFeO₃. GdFeO₃ (act as strong electron acceptors) inside the BiFeO₃–GdFeO₃ matrix acts as the trapping sites for electrons and produce a sufficient separation between charge carriers. It has been reported [55] that the electrons in conduction band of GdFeO₃, helps in the reduction of Gd³⁺ into Gd²⁺ species. The Gd²⁺ ions in the photocatalyst surface of can be re-oxidized into Gd³⁺ leads to generation superoxide radical ($\cdot O_2^-$) by reaction with oxygen. Superoxide radical ($\cdot O_2^-$) reacts with water (H₂O) molecules to form Hydroxyl radical ($\cdot OH$). Hydroxyl radicals ($\cdot OH$) and superoxide radicals ($\cdot O_2^-$) are the important candidate to degrade Methylene Blue (MB) into CO₂ and H₂O under visible light irradiation. Similarly, photogenerated holes can migrate from the valence band of GdFeO₃ to that of BiFeO₃. The movement of photogenerated electron–hole pairs are normally created by the internal electric field. Therefore, the photogenerated electrons and holes could be easily formed at the heterojunction formed between the BiFeO₃ and GdFeO₃ semiconductors. The series of steps involved in dye degradation are appended here under.



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

the fact that there exists an appreciable change in the crystalline strain upon loading GdFeO_3 with BiFeO_3 and it fairly agrees with the other results for the possible inclusion of GdFeO_3 in the BiFeO_3 matrix. UV-Vis-NIR studies on BiFeO_3 – GdFeO_3 suggest that band gap tuning found to have occurred due to the addition GdFeO_3 in the nanocomposite phase. The band gap energies of BiFeO_3 – GdFeO_3 was found as 1.8 eV, whereas the BiFeO_3 and GdFeO_3 figured 2.0 eV and 2.3 eV respectively. The reduction in the band gap energy values of BiFeO_3 – GdFeO_3 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 side 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 BiFeO_3 – GdFeO_3 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 BiFeO_3 and GdFeO_3 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.

Declarations

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 Gubendiran: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mohan Sriramalu: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- J.G. Yu, J.X. Low, W. Xiao, P. Zhou, M. Jaroniec, Enhanced photocatalytic CO_2 -reduction activity of anatase TiO_2 by coexposed {001} and {101} facets, *J. Am. Chem. Soc.* 136 (2014) 8839–8842.
- L. Shang, T. Bian, B. Zhang, D.H. Zhang, L.Z. Wu, C.H. Tung, Y.D. Yin, T.R. Zhang, Graphene-supported ultrafine metal nanoparticles encapsulated by mesoporous silica: robust catalysts for oxidation and reduction reactions, *Angew. Chem. Int. Ed.* 53 (2014) 250–254.
- H.G. Wei, D.W. Ding, X.R. Yan, J. Guo, L. Shao, H.R. Chen, L.Y. Sun, H.A. Colorado, S.Y. Wei, Z.H. Guo, Tungsten trioxide/Zinc tungstate bilayers: electrochromic behaviors, energy storage and electron transfer, *Electrochim. Acta* 132 (2014) 58–66.
- A. Mills, R.H. Davies, D. Worsley, Water purification by semiconductor photocatalysis, *Chem. Soc. Rev.* 22 (1993) 417–425.
- A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature* 238 (1972) 37–38.
- H. Mirabolghasemi, N. Liu, K. Lee, P. Schmuki, Formation of 'single walled' TiO_2 nanotubes with significantly enhanced electronic properties for higher efficiency dye-sensitized solar cells *Chem. Commun. Now.* 49 (2013) 2067–2069.
- H. Irie, K. Kamiya, T. Shibamura, S. Miura, D.A. Tryk, T. Yokoyama, K. Hashimoto, Visible light-sensitive Cu(II) -grafted TiO_2 photocatalysts: activities and X-ray absorption fine structure analyses, *J. Phys. Chem. C* 113 (2009) 10761–10766.
- M. Liu, X.Q. Qiu, M. Miyauchi, K. Hashimoto, Cu(II) oxide amorphous nanoclusters grafted Ti^{3+} -self-doped TiO_2 : an efficient visible light photocatalyst, *Chem. Mater.* 23 (2011) 5282–5286.
- M.,M. Momeni, Y. Ghayeb, Photochemical deposition of platinum on titanium dioxide-tungsten trioxide nanocomposites: an efficient photocatalyst under visible light irradiation, *J. Mater. Sci. Mater. Electron.* 27 (2015) 1062–1069.
- M.,M. Momeni, Y. Ghayeb, Preparation of cobalt coated TiO_2 and WO_3 – TiO_2 nanotube films via photo-assisted deposition with enhanced photocatalytic activity under visible light illumination, *Ceram. Int.* 42 (2016) 7014–7022.
- Mohamad Mohsen Momeni, Mahboubeh Mirhosseini, Maliheh Chavoshi, Growth and characterization of Ta_2O_5 nanorod and WTa_2O_5 nanowire films on the tantalum substrates by a facile one-step hydrothermal method, *Ceram. Int.* 42 (2016) 9133–9138.
- Y. Ghayeb, M.M. Momeni, M. Menati, Reduced graphene oxide/ Cu_2O nanostructure composite films as an effective and stable hydrogen evolution photocathode for water splitting, *J. Mater. Sci.: Materials* 28 (2017) 7650–7659.
- Mohamad Mohsen Momeni, Yousef Ghayeb, Zohre Ghonchehi, Fabrication and characterization of copper doped TiO_2 nanotube arrays by in situ electrochemical method as efficient visible-light photocatalyst, *Ceram. Int.* (2015) 8735, 8735–8714.
- Mohamad Mohsen Momeni, Zohre Nazari, Preparation of TiO_2 and WO_3 – TiO_2 nanotubes decorated with PbO nanoparticles by chemical bath deposition process: a stable and efficient photo catalyst, *Ceram. Int.* 42 (2016) 8691–8697.
- Mohamad Mohsen Momeni, Ghayeb Yousef, Fabrication and characterization of zinc oxide-decorated titaniananoporous by electrochemical anodizing-chemical bath deposition techniques: visible light active photocatalysts with good stability, *J. Iran. Chem. Soc.* 13 (2016) 481–488.
- Mohamad Mohsen Momeni, Mohaddeseh Hakimian, Kazempour Ali, In-situ manganese doping of TiO_2 nanostructures via single-step electrochemical anodizing of titanium in an electrolyte containing potassium permanganate: a good visible-light photocatalyst *Ceramics, International* 41 (2015) 13692–13701.
- Mohamad Mohsen Momeni, Ghayeb Yousef, Preparation of cobalt coated TiO_2 and WO_3 – TiO_2 nanotube films via photo-assisted deposition with enhanced photocatalytic activity under visible light illumination, *Ceram. Int.* (2016) 7014–7022.
- Mohamad Mohsen Momeni, Yousef Ghayeb, Zohre Ghonchehi, Visible light activity of sulfur-doped TiO_2 nanostructure photoelectrodes prepared by single-step electrochemical anodizing process, *Journal of Solid State* 19 (2015) 1359–1366.
- M.M. Momeni, M. Mirhosseini, M. Chavoshi, A. Hakimizade, The effect of anodizing voltage on morphology and photocatalytic activity of tantalum oxide nanostructure, *J. Mater.* 27 (2016) 3941–3947.
- Mohamad Mohsen Momeni, Study of synergistic effect among photo-, electro-, and sonoprocesses in photocatalyst degradation of phenol on tungsten-loaded titania nanotubes composite electrode, *Appl. Phys. A* 119 (2015) 1413–1422.
- M.M. Momeni, Y. Ghayeb, S. Gheibee, Silver nanoparticles decorated titanium dioxide-tungsten trioxide nanotube films with enhanced visible light photocatalytic activity, *Ceram. Int.* 43 (2017) 564–570.
- Mohamad Mohsen Momeni, Ghayeb Yousef, Synthesis and characterization of iron-doped titania nanohoneycomer5b and nanoporous semiconductors by electrochemical anodizing method as good visible light active photocatalysts, *J. Mater. Sci. Mater. Electron.* 26 (2015) 5509–5517.
- M.M. Momeni, Y. Ghayeb, A.A. Mozafari, Optical and photocatalytic characteristics of Ag 2 S/ TiO_2 nanocomposite films prepared by electrochemical anodizing and SILAR approach, *J. Mater. Sci.* 27 (2016) 11201–11210.
- F. Gao, X.Y. Chen, K.B. Yin, S. Dong, Z.F. Ren, F. Yuan, T. Yu, Z.G. Zou, J.M. Liu, Visible-light photocatalytic properties of weak magnetic BiFeO_3 nanoparticles, *Adv. Mater.* 19 (2007) 2889–2892.
- U.A. Joshi, J.S. Jang, P.H. Bors, J.S. Lee, Microwave synthesis of single-crystalline perovskite BiFeO_3 nanocubes for photoelectrode and photocatalytic applications, *Appl. Phys. Lett.* 92 (2008) 242106.
- F. Gao, Y. Yuan, K.F. Wang, X.Y. Chen, F. Chen, J.M. Liu, Preparation and photo absorption characterization of BiFeO_3 nanowires, *Appl. Phys. Lett.* 89 (2006) 102506.
- X.Y. Chen, T. Yu, F. Gao, H.T. Zhang, L.F. Liu, Y.M. Wang, Z.S. Li, Z.G. Zou, Application of weak ferromagnetic BiFeO_3 films as the photoelectrode material under visible-light irradiation, *Appl. Phys. Lett.* 91 (2007), 022114.
- R.A. He, S.W. Cao, P. Zhou, J.G. Yu, Recent advances in visible light Bi-based photocatalysts, *Chin. J. Catal.* 35 (2014) 989–1007.
- F. Niu, D. Chen, L. Qin, T. Gao, N. Zhang, S. Wang, Y. Huang, Synthesis of Pt/ BiFeO_3 heterostructured photocatalysts for highly efficient visible-light photocatalytic performances, *Sol. Energy Mater. Sol. Cell.* 143 (2015) 386–396.
- F. Niu, D. Chen, L. Qin, T. Gao, N. Zhang, S. Wang, Z. Chen, Y. Huang, Facile synthesis of highly efficient p–n heterojunction CuO/BiFeO_3 composite

- photocatalysts with enhanced visible-light photocatalytic activity, *ChemCatChem* 7 (2015) 3279–3289.
- [31] X. Wang, W. Mao, J. Zhang, Y. Han, C. Quan, Q. Zhang, T. Yang, J. Yang, X.A. Li, W. Huang, Facile fabrication of highly efficient g-C₃N₄/BiFeO₃ nanocomposites with enhanced visible light photocatalytic activities, *J. Colloid Interface Sci.* 448 (2015) 17–23.
- [32] T. Soltani, B.K. Lee, Sono-synthesis of Nano crystallized BiFeO₃/reduced graphene oxide composites for visible photocatalytic degradation improvement of bisphenol A, *Chem. Eng. J.* 306 (2016) 204–213.
- [33] Yathavan Subramanian, Venkatapathy Ramasamy, Ramesh Kumar Gubendiran, Gokul Raj Srinivasan, Durairajan Arulmozhi, Structural, Optical, Thermal and Photocatalytic dye degradation properties of BiFeO₃ – WO₃ nanocomposites, *J. Electron. Mater.* 47 (12) (2018) 7212–7223.
- [35] L. Jiang, S. Yang, M. Zheng, H. Chen, A. Wu, Synthesis and magnetic properties of nanocrystalline Gd₃Fe₅O₁₂ and GdFeO₃ powders prepared by sol–gel auto-combustion method, *Mater. Res. Bull.* 104 (2018) 92–96.
- [36] S. Husain, A.O. A. Keelani, W. Khan, Influence of Mn substitution on morphological, thermal and optical properties of nanocrystalline GdFeO₃ orthoferrite, *Nano-Structures & Nano-Objects* 15 (2018) 17–27.
- [37] V. Bedekar, V. Jayakumar, O.D. Manjanna, A.K. Tyagi, Synthesis and magnetic studies of nano-crystalline GdFeO₃, *Mater. Lett.* 62 (23) (2008) 3793–3795.
- [38] X. Li, Z.Q. Duan, Synthesis of GdFeO₃ microspheres assembled by nanoparticles as magnetically recoverable and visible-light-driven photocatalysts, *Mater. Lett.* 89 (2012) 262–265.
- [39] E.S. Baeissa, Environmental remediation of aqueous methyl orange dye solution via photocatalytic oxidation using Ag-GdFeO₃ nanoparticles, *J. Alloy. Comp.* 678 (2016) 267–272.
- [40] B. Sivakumar, S. Mohan, B. Subramanian, Experimental evidence for the carrier transportation enhanced visible light driven photocatalytic process in bismuth ferrite (BiFeO₃) one-dimensional fiber nanostructures, *J. Phys. Chem. C* 120 (2016) 18811.
- [41] S. Bharathkumar, M. Sakar, K. Rohith Vinod, S. Balakumar, Versatility of electrospinning on the fabrication of fibrous mat and mesh nanostructures of bismuth ferrite (BiFeO₃) and their magnetic photocatalytic activities, *Phys. Chem. Chem. Phys.* 17 (2015) 17745.
- [42] L. Li, X. Wang, Y. Lan, W. Gu, S. Zhang, Synthesis, photocatalytic and electrocatalytic activities of wormlike GdFeO₃ nanoparticles by a glycol-assisted sol–gel process, *Ind. Eng. Chem. Res.* 52 (2013) 9130–9136.
- [43] Jiangtao Wu, Zhaoxiong Xie, Lansun Zheng, Shaoyu Mao, Zuo-Guang Ye, Room-temperature ferromagnetic/ferroelectric BiFeO₃ synthesized by a self-catalyzed fast reaction process, *J. Mater. Chem.* 20 (2010) 6512–6516.
- [44] P.D. Dimple, B.P. Mandal, M.D. Mukadam, S.M. Yusuf, A.K. Tyagi, Improved magnetic and ferroelectric properties of Sc and Ti doped multiferroic nano BiFeO₃ prepared via sonochemical synthesis, *Dalton Trans.* 43 (2014) 7838.
- [45] S. Mathur, H. Shen, N. Lecerf, A. Kjekshus, H. Fjellvag, G.F. Goya, Nanocrystalline orthoferrite GdFeO₃ from a novel heterobimetallic precursor, *Adv. Mater.* 14 (2014) 1405.
- [46] V. Mote, Y. Purushotham, B. Dole, Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles, *Journal of Theoretical and Applied Physics* 6 (1) (2016) 6.
- [47] D. Moitra, B.K. Ghosh, M. Chandel, N.N. Ghosh, Synthesis of a BiFeO nanowire-reduced graphene oxide based magnetically separable nanocatalyst and its versatile catalytic activity towards multiple organic reactions, *RSC Adv.* 6 (2016) 97941–97952.
- [48] A.A. Kokhanovsky, Physical interpretation and accuracy of the Kubelka–Munk theory, *J. Phys. D Appl. Phys.* 40 (2007) 2210–2216.
- [49] D. Jalandhara, G. Singh, K. Yadav, Effect of Sintering Temperature on the Optical Properties of BiFeO₃ Nanoparticles, 2016.
- [50] N.D. Ngoc, D.L. Minh, C.P. Ngoc, D.D. Trung, H.C. N. Thi, B.N. Quang, L.D. Thi, Low-temperature synthesis and investigations on photocatalytic activity of nanoparticles BiFeO₃ for methylene blue and methylene orange degradation and some toxic organic compounds, *Adv. Nat. Sci. Nanosci. Nanotechnol.* 7 (2016), 045003.
- [51] F. Lv, Y. Zhang, X. Chen, Y. Ma, Composition and fluorescence of gadolinium (III) acetylacetonate derivatives by solvothermal method, *Int J Opt Photonic Eng* 2 (2017) 005.
- [52] Geo George Philip, Anitha Senthambizhan, Thirupathur Srinivasan Natarajan, Gopalakrishnan Chandrasekaran, Helen Annal Therese, The effect of gadolinium doping on the structural, magnetic and photoluminescence properties of electrospun bismuth ferrite nanofibers, *Ceram. Int.* 41 (2015) 13361–13365.
- [53] L. Beránek, An examination of the Langmuir–Hinshelwood model using ion exchange catalysts, *Catal. Rev.* 16 (1977) 1–35.
- [54] S.G. Bratsch, Revised Mulliken electronegativities: I. Calculation and conversion to Pauling units, *J. Chem. Educ.* 65 (1988) 34.
- [55] P. Tang, Y. Hu, T. Lin, Z. Jiang, C. Tang, Preparation of nanocrystalline GdFeO₃ by microwave method and its visible-light photocatalytic activity, *Integr. Ferroelectr.* 153 (2014) 73–78.
- [56] D.P. DePuccio, P. Botella, B. O'Rourke, C.C. Landry, Degradation of methylene blue using porous WO₃, SiO₂–WO₃, and their Au-loaded analogs: adsorption and photocatalytic studies, *ACS Appl. Mater. Interfaces* 7 (3) (2015) 1987–1996.
- [57] Yunhui Si, Yayun Li, Jizhao Zou, Xinbo Xiong, Xierong Zeng, Ji Zhou, Photocatalytic performance of a novel MOF/BiFeO₃ composite, *Materials* 10 (2017) 1161.
- [58] Abdul Halim Abdullah, Wan Tze Peng, Mohd Zobir Hussein, Degradation of methylene blue dye by CuO–BiVO₄ photocatalysts under visible light irradiation, *Malaysian Journal of Analytical Sciences* 20 (2016) 1338–1345.