



Precipitation Method and Sonication Technique for Advanced Superiority of Nanospherical BiFe₂O₃ and its Multi-Applications

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In this work, a modified BiFe₂O₃ nanomaterial was prepared using a combination of co-precipitation and sonication methods. High-resolution scanning electron microscopy (HRSEM) results revealed a nanospherical shaped structure. The energy dispersive X-ray analysis (EDX) analysis confirmed that Bi, Fe and O are present in the BiFe₂O₃ nanomaterial. The photoluminescence analysis also confirmed the presence of bismuth in the BiFe₂O₃ nanomaterial. The recombination of electron-hole pairs in Fe₂O₃ transpires when the electrons and holes were transferred between Bi and Fe₂O₃ nanomaterials. The UV-Vis DRS analysis revealed that the nanomaterial decrease band gap energy and increased the photoenergy. The modified BiFe₂O₃ was successfully used as multi-functional materials, such as a photocatalytic material for the photodegradation of Rhodamine B and Rhodamine 6G dyes, antibacterial agent and as improved dye sensitized solar cells (DSSCS).

Keywords: BiFe₂O₃ nanomaterial, Photocatalytic activity, Antibacterial activity, Rhodamine B, Rhodamine 6G, DSSCS.

INTRODUCTION

Large amounts of attention are focused on the perovskite materials with the general formula ABX₃ or ABO₃, where 'A' and 'B' are two cations of different sizes and 'X' is an anion that bonds to both, due to their many desirable properties and found its applicability in various fields like electrochemical, wastewater treatment, magnetite, catalysis, biomedicines, *etc.* [1-4]. In addition to study the chemical degradation, perovskite structures' electrochemically driven ion evolution behaviours have gained a lot of interest because of their one-of-a-kind features and applications [5-7].

Recent advances in bismuth ferrite nanoclusters seem to be a good semiconductor material for eliminating a wide range of dyes since they can handle a wide range of frequencies, absorb a lot of visible light and are stable. When thin sheets of bismuth ferrite are changed, there is lots of the improvement in the properties happens [8-10]. At the nanoscale, bismuth ferrite materials exhibit new physical properties, which are different from what they possess in bulk or as a thin film [11-14].

The synthetic method has a significant impact on the chemical, morphological and the optical properties of perovskite materials, as is well known. The crystal structure and the shape of the

samples are also altered by the different synthetic routes [15]. Early in 1967, Achenbach *et al.* [16] reported a single phase polycrystalline BFO *via* solid-state reaction of BiO and FeO at < 700 °C. However, this method has some drawbacks, including a high reaction temperature, big particle size and the existence of contaminants. Alternatively, new methods *e.g.* chemical coprecipitation [17,18], hydrothermal [19], solvothermal [20], sonochemical [21], microemulsion [22], polyacrylamide gel [23], ferrioxalate [24], simple sol-gel [25], combustion synthesis [26], molten salt [27], tartaric acid assisted gel strategy [28], polymeric precursor [29] and mechanochemical synthetic route [30] are nowadays used commonly for the synthesis of bismuth ferrite nanopowders.

In this study, a broad BiFe₂O₃ nanomaterial was prepared using a combination of co-precipitation and sonication methods approach for producing consistent BiFe₂O nanomaterial. The prepared nanomaterial were characterized from HR-SEM, EDX, HR-TEM, XRD, photoluminescence spectroscopy and UV-Vis DRS analysis. Moreover, modified BiFe₂O₃ was successfully employed as an antibacterial agent, photocatalytic photodegradation of Rhodamine B and Rhodamine 6G dyes and enhanced dye sensitized solar cells (DSSCS).

EXPERIMENTAL

Ammonia solution, conc. nitric acid, bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], ferric chloride hexahydrate [$(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$], FTO-plate, Rhodamine B and Rhodamine 6G dyes were acquired from Sigma-Aldrich and used as received. Anthocynin dye was generated from the natural flower extract solution, ethanol solution and used as such. All the glasswares were acid washed before being completely washed with distilled water. Deionized water and ordinary water were used as controls throughout the experiment, with deionized water being used in the degradation processes.

Synthesis of Bi doped Fe_2O_3 : A simple co-precipitation process and sonication technique were used to prepare bismuth doped Fe_2O_3 nanomaterial. Ferric chloride hexahydrate (3 g) was dissolved in 100 mL of deionized water (solution A) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 M) was dissolved in 50 mL of deionized water (solution B). Under vigorous stirring, solution B was mixed into solution A dropwise manner. This precursor mixture was agitated at room temperature for 30 min before being adjusted to $\text{pH} = 9$ with ammonia solution. The resulting solution was again agitated for 3 h before being ultrasonicated for 40 min. The resulting precipitate was filtered and rinsed with distilled water followed by ethanol. The precipitate was then collected, dried for 15 h at 100°C in an oven and then calcined in a muffle furnace at 500°C for 4 h.

Characterization: The structural characterization of the deposited films was reported using Shimadzu-6000 (monochromatic $\text{CuK}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). The XRD patterns were identified in two intervals of 10° to 90° with 0.05° increments. The HR-SEM was used to investigate the surface morphology (JEOL-JES-1600). At 25°C , the EDX assessment trials were carried out on an FEI Quanta FEG 200 apparatus equipped with an EDX analyzer with transmissions with high resolution. The HR-TEM images were captured using a JEOL-JEM-2010 UHR system with a lattice image resolution of 0.14 nm and a 200 kV acceleration voltage. A Perkin-Elmer LS 55 fluorescence spectrometer was used to capture photoluminescence (PL) spectra at room temperature, while a Hitachi-U-2001 spectrophotometer was used to measure ultraviolet and visible (UV-Vis) absorbance spectra throughout a wavelength range of 800-200 nm using a quartz cell with a 10 mm optical path length. The photovoltaic evaluation of the prepared nanomaterial was done by recording the photocurrent voltage (I-V) curve under Ampere metres (A.M.) at 1.5 (100 Mw/cm²) light.

RESULTS AND DISCUSSION

Surface topography: The micrograph of calcined 500°C prepared Bi doped Fe_2O_3 nanomaterial consisted of well-defined nanospherical like structure (Fig. 1a), which also clearly exhibited homogeneous uniform distribution, thus, the surface morphology has high efficiency of photocatalytic activity. Fig. 1b shows the clearly sharp high density of Fe and O, the decreasing density of Bi and the totally homogeneous circulation of Bi, Fe and O indicates the purity of the nanomaterial, when analyzed with energy dispersive X-ray spectroscopy (EDX) were carried out.

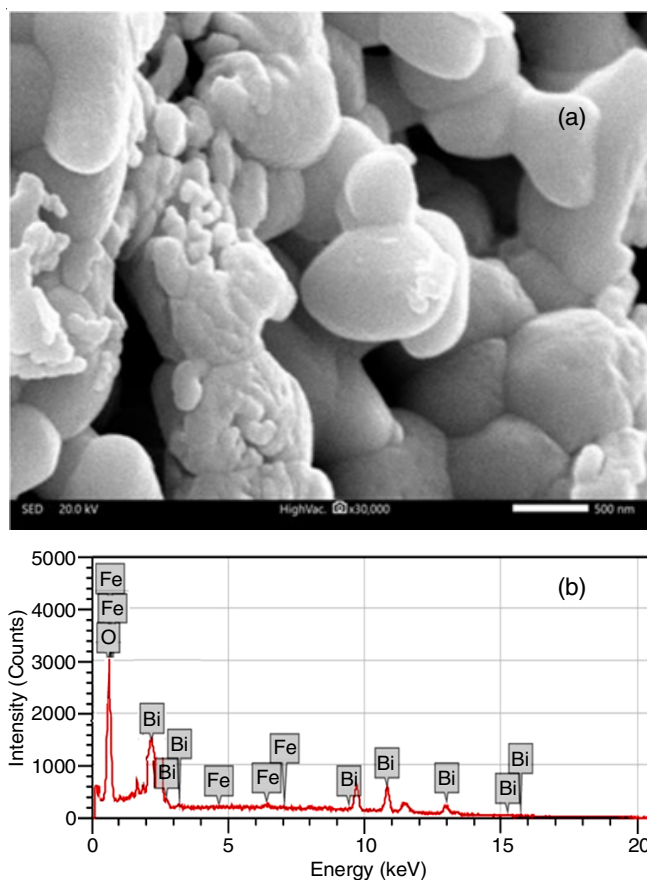


Fig. 1. SEM analysis of (a) SEM image BiFe_2O_3 nanomaterial and (b) EDS analysis

The prepared BiFe_2O_3 nanomaterial consisted of well-defined nanospherical like structure as exhibited from Fig. 2a, whereas Fig. 2b showed the number of bright rings, which correspond to the polycrystalline nature. Fig. 2c represented a 3D structured by selecting and highlighting electron area, whereas Fig. 2d shows a average particle angle size range distribution 28 nm and has average particle maximum size range distribution of 51 nm, which was calculated using Image J Viewer software.

XRD studies: The prepared BiFe_2O_3 nanomaterial annealed at 500°C for 4 h revealed the sharp peaks presents its high crystallinity structure. The prepared bismuth doped Fe_2O_3 exhibit the XRD peaks at 22.5° , 24.8° , 30.1° , 32.1° , 33.6° , 36.2° , 40.4° , 47.2° , 52.0° and 56.1° are indexed to the (003), (101), (110) planes (JCPDS no. 36-1451, 44-1246 and 79-0206) [19, 20], moreover the additional small peaks at 28° and 32° conformed that bismuth is well doped onto Fe_2O_3 [21-23] (Fig. 3a-b). The crystal structures of Fe_2O_3 and BiFe_2O_3 nanomaterials were FCC and its particle size were found to be 21 and 16 nm, respectively as calculated from the Debye-Scherrer's equation.

Photoluminescence (PL) studies: Fig. 4 shows the PL spectra of Fe_2O_3 and as-prepared BiFe_2O_3 nanomaterial at the excitation wavelength of $\lambda = 320 \text{ nm}$. For both materials, the emissions at 330, 360, 380, 420, 440 and 540 nm are same and although different intensities was obtained. The Fe_2O_3 nanomaterial was high at 500 nm, while in case of BiFe_2O_3 nanomaterial, a low intensity was observed, which demonstrated the

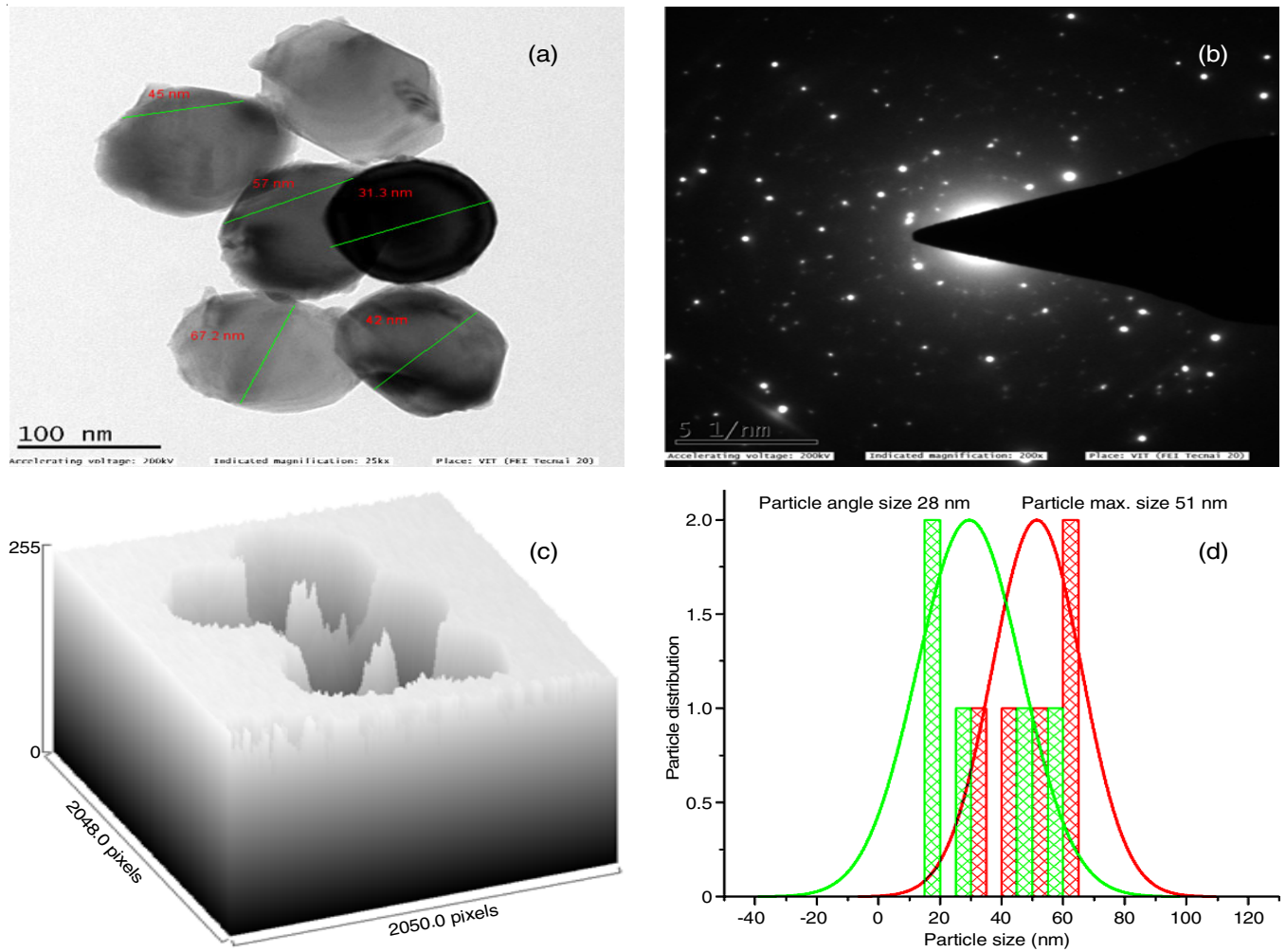


Fig. 2. HR-TEM micrographs; (a) image of BiFe₂O₃, (b) SAED pattern, (c) image profile 3D structure and (d) average particle angle size 28 and particle max size 51 nm by selected particle length area highlighted in HR-TEM image (a)

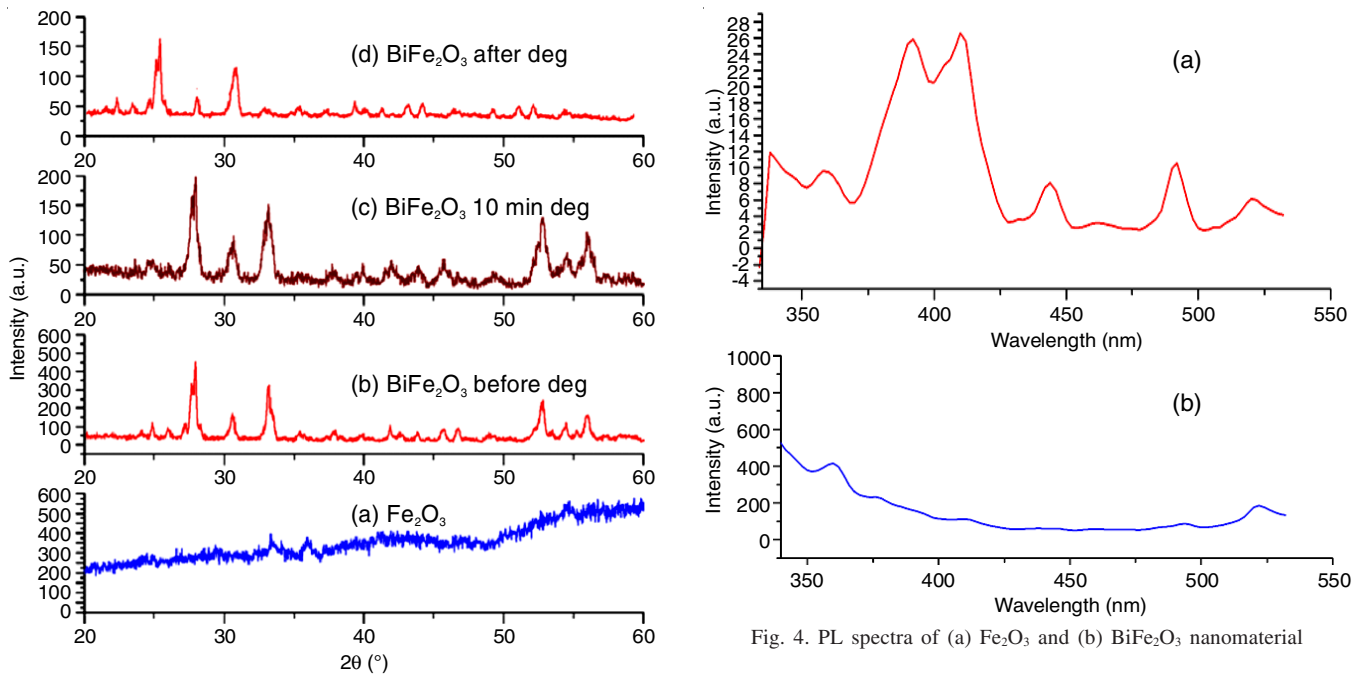


Fig. 3. XRD analysis of (a) Fe₂O₃, (b) BiFe₂O₃, (c) BiFe₂O₃ after 10 min degradation and (d) BiFe₂O₃ after deg. nanomaterial

Fig. 4. PL spectra of (a) Fe₂O₃ and (b) BiFe₂O₃ nanomaterial extending life-times of electrons and holes resulting in the enhanced optical, electrical and microbiological performances [26,27].

UV-Vis-DRS studies: The UV-Vis-DRS analysis of the synthesized Fe_2O_3 and BiFe_2O_3 nanomaterials revealed the UV and visible absorption in the 200-800 nm range. The Kubelka-Munk (KM) function was used to transform the DRS spectra (R). The direct band gap of the synthesized material has been determined from the Tauc plot using UV-Vis-DRS spectra of synthesized Fe_2O_3 and BiFe_2O_3 nanomaterial. A blue shift observed in Fe_2O_3 nanomaterial was due to the size effect (Fig. 5). The band gap energies of Fe_2O_3 and BiFe_2O_3 nanomaterials were found to be 2.3 and 2.05 eV, respectively. These findings suggested that doping nanomaterials with low band gap energy cause higher light absorption [31-34].

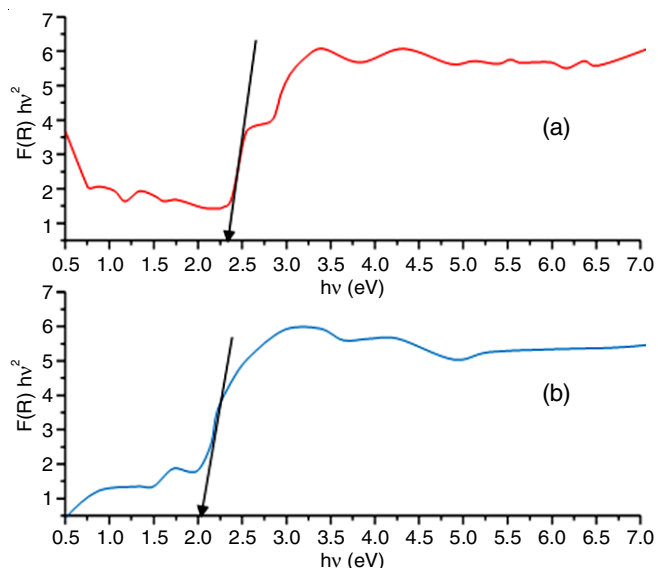


Fig. 5. UV-Vis DRS of plot of transferred Kubelka-Munk vs. energy of light absorbed of (a) Fe_2O_3 and (b) BiFe_2O_3 nanomaterial

Photocatalytic activity: The photocatalytic degradation of prepared Fe_2O_3 and BiFe_2O_3 nanomaterial on rhodamine B (Rh B) and rhodamine 6G (Rh 6G) dyes were exposed to UV light at 365 nm for 50 min at the span of every 10 min. The efficiency degradation of dye under different conditions *e.g.* (a) dye + UV + No catalyst; (b) dye + BiFe_2O_3 + dark; (c) dye + Fe_2O_3 + UV and (d) dye + BiFe_2O_3 + UV analysis results in the degradation of rhodamine 6G dye (0, 1, 2, 3, 5.5 and 8%), (0, 2, 4, 6, 9 and 13%), (0, 8, 15, 28, 39 and 54%) and (0, 11, 24, 50, 78 and 96%), respectively (Fig. 6a-d). Under the same concentration and dosage catalyst amount, the photocatalytic degradation efficiency is very high for BiFe_2O_3 nanomaterial as compared to undoped Fe_2O_3 nanomaterial. Similarly, the photocatalytic activity for rhodamine B (Rh B), the result patterns are almost same in this case also (Fig. 7a-d). However, the prepared BiFe_2O_3 nanomaterial degrade rhodamine 6G (Rh 6G) dye more efficiently than rhodamine B (Rh B) dye.

Influence of parameters

Effect of catalyst loading effect: As can be observed from Fig. 8, the photodegradation efficiency enhanced with an increase in amount up to 0.08 g/50 mL and then significantly decreased with catalyst loadings of 0.04, 0.08 and 0.1 g/50 mL. Thus, catalyst loading of 0.08 g had the best photocatalytic activity.

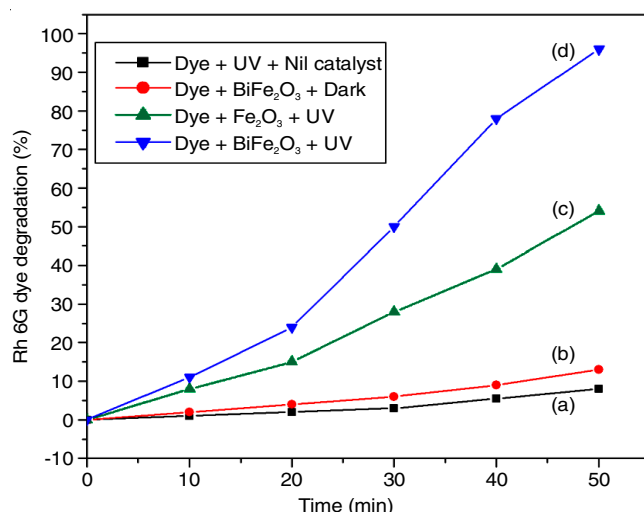


Fig. 6. Effect of photocatalytic efficiency of Rh 6G dye under UV-light irradiation (A) by (a) Dye + UV + Nil catalyst, (b) Dye + BiFe_2O_3 + Dark, (c) Dye + Fe_2O_3 + UV and (d) Dye + BiFe_2O_3 + UV analysis

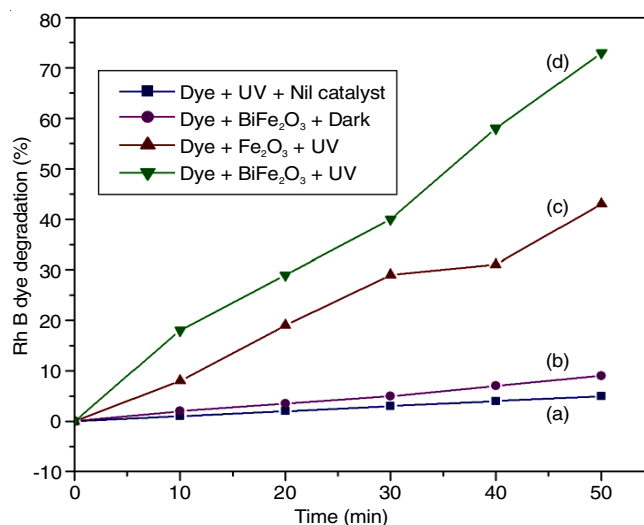


Fig. 7. Effect of photocatalytic efficiency of Rh B dye under UV-light irradiation (A) by (a) Dye + UV + Nil catalyst, (b) Dye + BiFe_2O_3 + Dark, (c) Dye + Fe_2O_3 + UV and (d) Dye + BiFe_2O_3 + UV analysis

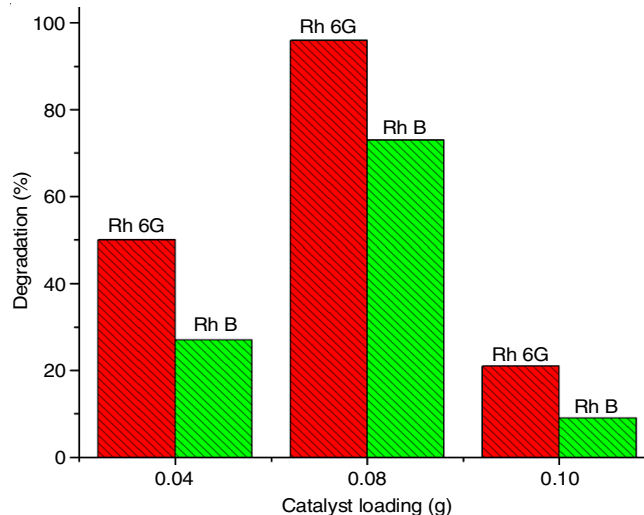


Fig. 8. Effects of catalyst loading (0.04, 0.08 and 0.1 g): Rh 6G and Rh B dye under UV-light irradiation at 365 nm by BiFe_2O_3 nanomaterial

however, with further excessive dosage, UV-light diffusion in the particles decreases [35].

Effect of concentrations: Fig. 9 shows that at the 1×10^{-4} M, Rh 6G and Rh B dyes achieved the maximum degradation efficiency of 96% and 73%, respectively. Upon further increasing the concentration (2×10^{-4} M and 3×10^{-4} M), the percentage of photodegradation activity decreases drastically for both dyes. These results indicated that at high concentration, the catalyst surface area is less available due to the presence of higher dye molecules, which results in the reduction of the photocatalytic activity.

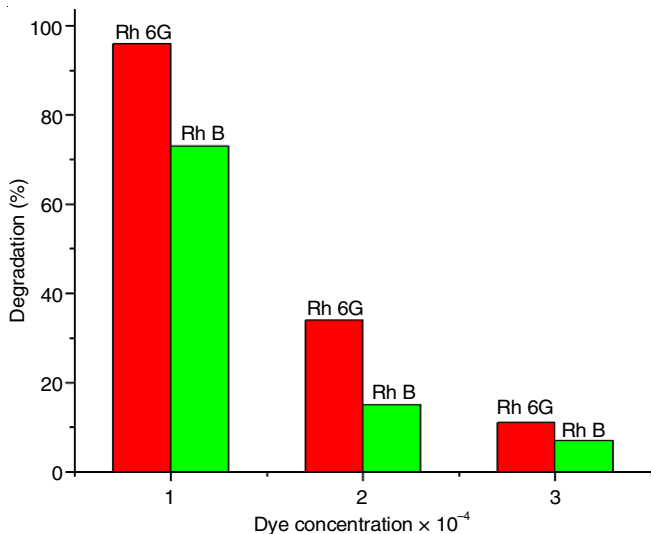


Fig. 9. Effects of different concentrations (1×10^{-4} , 2×10^{-4} and 3×10^{-4} M): Rh 6G and Rh B dye under UV-light irradiation at 365 nm by BiFe₂O₃ nanomaterial

Reusability: The photocatalyst's stability and reusability are critical aspects of the catalytic process in the industrial applications. The photocatalytic degradation capabilities of prepared BiFe₂O₃ photocatalyst were studied by repeating photocatalytic degradation tests with Rh 6G and Rh B dyes five times. The photocatalysts were extensively washed with water after each cycle and a fresh solution of Rh 6G and Rh B dyes was tested before each photocatalytic run in the photo-reactor under UV light. A satisfactory degradation efficiency was achieved within 0-50 min (100, 95, 93, 86 and 86%) as observed in Fig. 10 upto 5 cycles. In comparison to the total dye degradation, catalyst efficiency dropped after the fourth cycle.

Mechanism of photocatalytic efficiency: The mechanism of photocatalytic efficiency as follows:

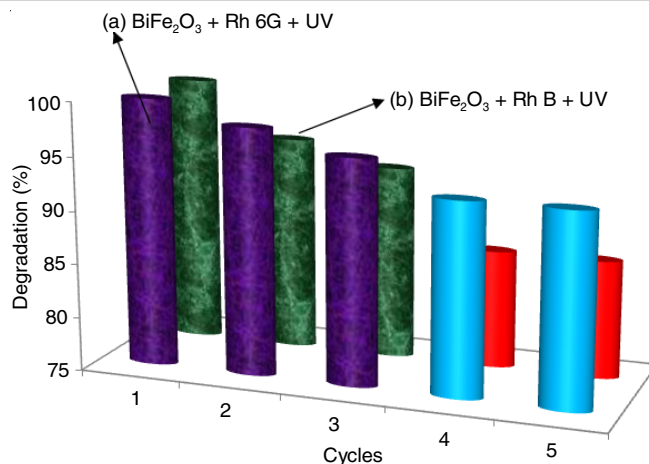
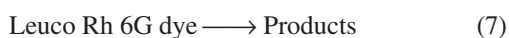
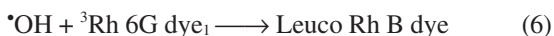
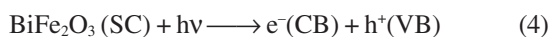
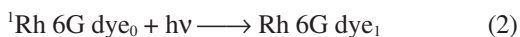
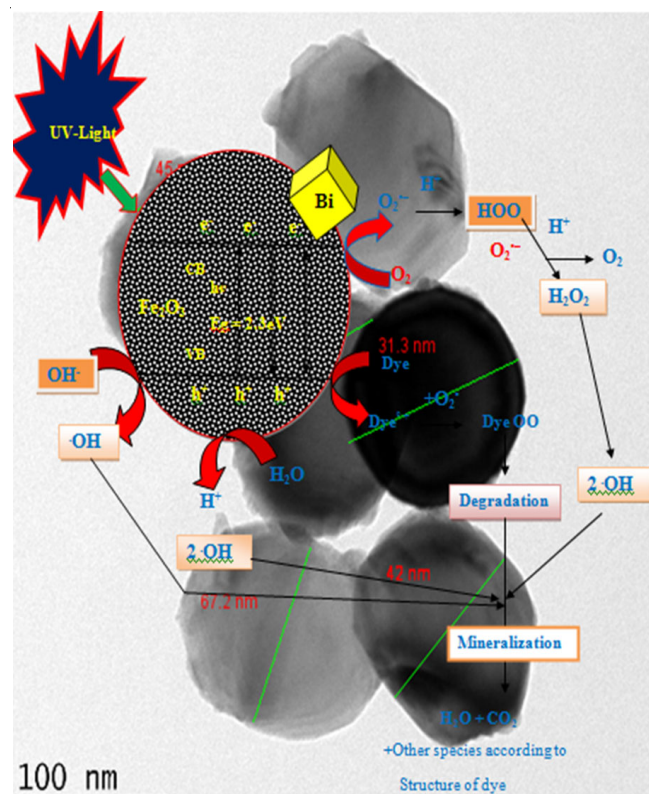


Fig. 10. Reusability of catalyst; Rh 6G and Rh B dye under UV-light irradiation at 365 nm by BiFe₂O₃ nanomaterial

Rhodamine 6G (Rh 6G) absorbs photons irradiated from the wavelength and generates an energetic singlet state. It also travels *via* ISC or intersystem crossover to give it an extra established triplet state. This energy was also used by BiFe₂O₃ semiconductor or SC to excite its electron from the valence band to the conduction band. A proton can be extracted from ${}^-\text{OH}$ by a hole (h^+) present in the semiconductor's valence band resulting in the formation of $\cdot\text{OH}$. The Rh 6G dye will be oxidized to its leuco-form by this $\cdot\text{OH}$, which may eventually decay to smaller products. The presence of an $\cdot\text{OH}$ scavenger (2-propanol) significantly reduced the rate of degradation of Rh B dye indicating that $\cdot\text{OH}$ is an active oxidizing species in the degradation of Rh B dye as shown in **Scheme-I** [36].



Scheme-I: Schematic representation: Mechanism of BiFe₂O₃ nanomaterial

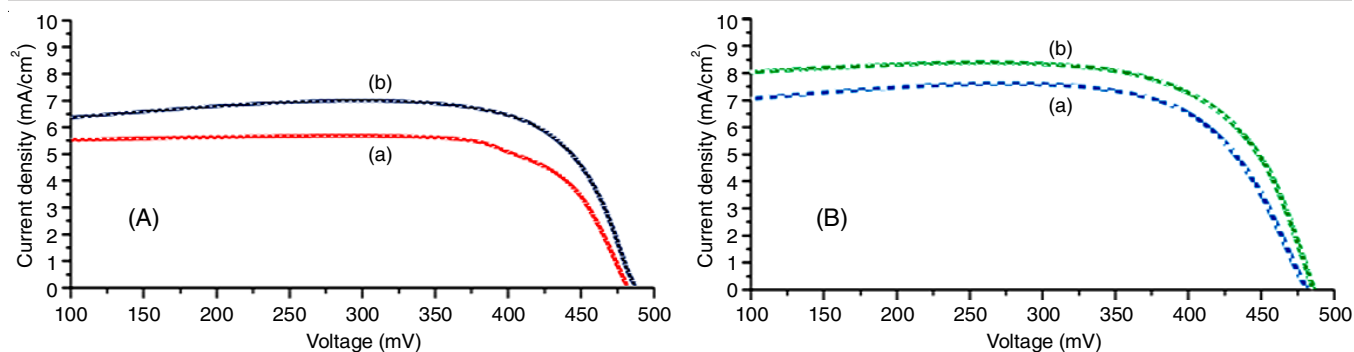


Fig. 11. Current density-voltage (J-V) curves from the DSSC's made-up from fabricated from (A) Rosa^b flower extract (anthocyanins) dye based sensitized solar cell (DSSCs) (a) Fe₂O₃ and (b) BiFe₂O₃ nanomaterial and (B) Coffee^b leaf based extract (anthocyanins) dye based sensitized solar cell (DSSCs) (a) Fe₂O₃ and (b) BiFe₂O₃ nanomaterial

Dye sensitized solar cells (DSSCs)

DSSCs based on rosa flowers and coffee leaves extract:

The prepared BiFe₂O₃ was also applied to make a standard solar cell based on rosa flower extract, which gives the high electroefficiency from short-circuit current density as compared to Fe₂O₃ as indicated from the results that rosa flowers based extract BiFe₂O₃ produce J_{sc} value of 8 mA/cm², whereas Fe₂O₃ produce J_{sc} value of 7.1 mA/cm². Similarly, using coffee leaf extract based dye sensitized solar cell (DSSCs), BiFe₂O₃ produce J_{sc} value of 6.4 mA/cm², while Fe₂O₃ produce J_{sc} value of 5.5 mA/cm² (Fig. 11).

Antibacterial activity: The disc diffusion method was used in this investigation to evaluate the Fe₂O₃ and BiFe₂O₃ nanomaterial's antibacterial efficacy against human bacterial pathogens (*Staphylococcus aureus* and *Escherichia coli*). The antibacterial activity results of undoped Fe₂O₃ and doped BiFe₂O₃ nanomaterials is shown in Fig. 12. The undoped Fe₂O₃ and doped BiFe₂O₃ nanomaterials are active almost equally to the standard ciprofloxacin against Gram-positive and Gram-negative

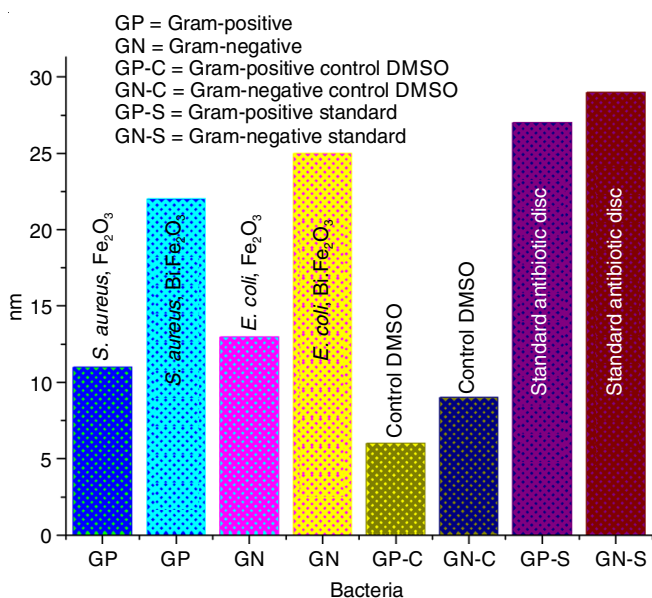


Fig. 12. Antibacterial activity [disc diffusion method]: (a) *Staphylococcus aureus* and (b) *Escherichia coli* investigation of prepared (a) Fe₂O₃ and (b) BiFe₂O₃ nanomaterial showed activity against both Gram-positive & Gram-negative strains

pathogenic organisms. Evaluation of BiFe₂O₃ nanomaterial as antibacterial agent is attributed due to the high value of electron holes charge separation through low band gap energy, which causes a decrease in the charge recombination and results in the significant antibacterial activity [37].

Conclusion

A combined co-precipitation and sonicated method was used to synthesize BiFe₂O₃ nanomaterial successfully. The HR-SEM analysis revealed that BiFe₂O₃ has a well-defined nanospherical like form. The produced spherical-like structure of the BiFe₂O₃ nanomaterial shows the strong photocatalytic activity when compared to Fe₂O₃ as confirmed through photoluminescence studies. The UV-Vis DRS results revealed the low band gap energy, making it useful as photocatalyst material for the degradation of rhodamine 6G and rhodamine B dyes. The generated nanomaterial was found to be stable and reusable after a feasible five time process. Furthermore, BiFe₂O₃ nanomaterial also exhibited the similar antibacterial activity towards *Escherichia coli* and *Staphylococcus aureus* bacterial pathogens as compared to standard ciprofloxacin.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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