Critical review: Bismuth ferrite as an emerging visible light active nanostructured photocatalyst

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\section*{Abstract}

Photocatalytic technology has got great attention in recent days because of increasing problems of energy crisis and environmental pollution. Many semiconductor photocatalyst has been investigated, among them BiFeO\textsubscript{3} has got great attention due to its unique morphological structural and multiferroic properties. In this review, detailed discussion of crystal structure, electronic band structure, degradation mechanism, different factors affecting on degradation efficiencies of BiFeO\textsubscript{3} has been included. The different fabrication techniques and possibilities of improvement photoactivity of BiFeO\textsubscript{3} with different modification were also discussed. This review also gives a broad overview of BiFeO\textsubscript{3} as visible light photocatalysts, summarizing the present state of research work and providing some useful understandings for their future progress.

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1. Introduction

About 1.39 cu.km water has been found on earth, from which 2.5% is fresh water and only 0.29–0.49% is available for drinking water [1]. So, in accordance with this ratio, there is an obvious need to recycle the polluted water. Water contamination problem has got a significant challenge and many of the researchers are trying to figure out some better ways to cope with this problem [2–4]. The industrial effluents such as, pharmacy, textile and rubber wastes are becoming a severe
environmental damage [5]. The textile industries dyes cause cancer and also hazardous for aquatic life [6,7]. Some waste water-treatment processes are, (i) sedimentation, (ii) filtration, (iii) coagulation (iv) ion floating, (v) absorption [8–11].

Now-a-days, an advanced technique is also making its name in treatment of polluted water, known as “advanced oxidation process”. This method includes oxidation technique of effluents (pollutants) with hydroxyl ions (\(\text{OH}^-\)) [12,13]. The major steps are, (a) formation of hydroxyl ions \(\text{OH}^-\), (b) hydroxyl radicals attack on the target molecules of pollutants and cause their breakdown into smaller substances until complete mineralization occur. So, it got attention due to its ability to destroys harmful organic pollutants and avoid conversion of pollutants into harmful product [14]. In developing countries are using this technique on smaller scale. Some advanced oxidation processes are, (i) ozonation technique, (ii) sonolysis, (iii) fenton process, (iv) photo-fenton process, (v) photocatalysis, (vi) bio-degradation, (vii) UV-photocatalysis [15,16]. Among them, photocatalysis is an efficient technique because it uses solar energy for the treatment of organic pollutants.

The mechanism of photocatalysis is described in Eqs. (I–V), when the incoming light falls on target semiconductor (having energy greater or equal to band-gap), then electron and hole pair is generated and they travel towards the photocatalyst's surface and redox reactions occur with the compounds that are bound on the surface of that catalyst. The water molecules get oxidized by the holes to produce hydroxyl radicals and then generated electrons reduced the dissolved oxygen in water to produce \(\text{O}_2^-\).

\[
\text{Photocatalyst} + \text{hv} \rightarrow e^- + h^+ (I)
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{OH} + \text{H}^+ (II)
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- (III)
\]

The hydroxyl and \(\text{O}_2^-\) ions caused the redox reactions of the dye molecules and produce smaller compounds and this cause dye de-colorization. The superoxide anion radicals are produced which reacts with \(\text{H}^+\) ions and produce more \(\text{OH}^-\) radicals.

\[
\text{OH} + \text{dye} \rightarrow \text{dye(oxidation)} (IV)
\]

\[
e^- + \text{dye} \rightarrow \text{dye(reduction)} (V)
\]

Photocatalysis of dye substances is not possible without dissolved oxygen and \(\text{H}_2\text{O}\) molecules because they cause the production of \(\text{OH}^-\) radicals [2]. The whole process of photocatalysis is shown in Fig.1. When the light of energy falls on the surface of semiconductor, electrons and hole pairs are produced. Different semiconductors such as, \(\text{ZnS}, \text{CdS}, \text{ZnO}, \text{TiO}_2\) having photosensitive properties have also been studied for photocatalytic application. But, the major problem is that most of the semiconductors have wide band-gap which only absorbs light energy in UV-reign which is only 4% of sunlight.

Another problem is the fast recombination of electrons and holes, which also lowers the efficiency of photocatalyst [18,19]. For photocatalysis, a new group of such materials, which came in the class of materials having perovskite structure, is also getting importance now days [20]. The perovskite structure have general formula, \(\text{ABX}_3\) [21] where, A and B-sites are two different sized cations, in which A is normally bigger than B-cation. These cations help to understand the properties of the crystals. X-anion can be oxide or halide. The ideal \(\text{ABX}_3\) perovskite materials possesses cubic symmetry with space group \(\text{Pm3m}\), in which, B cation is 6 fold coordinated and A cation is 12 fold cubo octahedral co-ordinated surrounded by an octahedron of X-anions. This investigation only employs to the materials having ABO\(_3\) structures, as described in Fig. 2. The ABO\(_3\) perovskite substances shows lattice distortions which results in transfer of crystal phases in sequence such as, monoclinic, tetragonal, triclinic and orthogonal phases. The different degree of orientation results in various optical and electronic properties.

ABO\(_3\) materials are better than other photosensitive semiconductors for photocatalysis due to wide range band-gap, which can also altered and photo-physical properties of A and B cations [23]. Some photocatalyst that have been studied yet, such as, (i) ferrites: LaFeO\(_3\), BiFeO\(_3\), GdFeO\(_3\), (ii) tantalates: AgTaO\(_3\), NaTaO\(_3\), KTaO\(_3\), (iii) titanates: SrTiO\(_3\), CdTiO\(_3\), NiTiO\(_3\), GoTiO\(_3\), CaTiO\(_3\), FeTiO\(_3\), BaTiO\(_3\), (iv) some of the others are LaCaO\(_3\) and LaNiO\(_3\) [24–35]. However, BiFeO\(_3\) materials has got attention due to following properties: (i) band-gap exists in visible-light region, (ii) multiferroic existence at room temperature (25°C), which supports in separation of cations and...
anions efficiently and, (iii) high chemical stability [36–41]. This review covers a comprehensive explanation on photocatalytic degradation of different organic compounds by BiFeO₃-based nanostuctures and possible ways of enhancing photocatalytic performance.

1.1. Crystal and band structure of BiFeO₃

BiFeO₃ was discovered in 1950’s. It showed an antiferromagnetic and ferromagnetic properties with Neel temperature of \(T_N = 647\) K for antiferromagnetic and a ferroelectric Curie temperature of \(T_C = 1103\) K [42,43]. The grounded BiFeO₃ in bulk phase with a space group R3c (a = 5.58 Å and c = 13.9 Å) has rhombohedral structure, at room temperature (25 °C) [44]. At room temperature, the unit cell has a rhombohedral angle, \(\alpha_{th}\), of ca. 89.3–89.48° and the lattice parameter is 3.965 Å, having ferroelectric polarization [45]. It showed multiferroic properties at room temperature (25 °C). It exhibits a Neel temperature of 370 °C and showed a curie temperature of 830 °C. The hexagonal frame of reference is another description of BiFeO₃ unit cell, where the c-axis is \(\parallel\) to diagonal of the cubic such as, [001]\(_{\text{hexagonal}}\) \(\parallel\) [111]\(_{\text{perovskite}}\). The values for thermal expansion coefficient are varied from \(6.5 \times 10^{-6}\) to \(13 \times 10^{-6}\) K\(^{-1}\), which confirmed that it may not be isotropic or linear [46]. A key factor for structural point of view is the angle of rotation for the oxygen octahedra. The cubic perovskite has an angle of 0° which completely matched with ionic sizes. In order to check the matching of ionic into perovskite unit cell, here is the formula: \((r_Bi + r_O)/l\), where \(l\) is the length of octahedral and \(r\) is the ionic radii.

The fabrication process of BiFeO₃–based material is simple at room temperature, but sometimes they showed impurities such as, Bi₂FeO₉ and Bi₂5FeO₉₉ [47,46]. It also showed the magnetoelectric coupling property which provides a wide range of properties due to which it can be used in non-volatile memory, piezoelectric devices, sensors and spintronics [49–55]. The band-gap of BiFeO₃ material also lies in the visible-light region in the solar spectrum, which enhance its worth in fabrication of photovoltaics and photocatalysis [56–60]. The X-ray diffraction (XRD) patterns of BiFeO₃ demonstrated that the peaks at (101), (004), (200), (105), (211) and (204) confirmed the rhombohedral phase, as shown in Fig. 3a.

It’s unit cell can also be represented by a hexagonal frame of reference, Fig. 3b.

Moreover, some researchers reported a pseudo cubic frame of reference which has also been used for photocatalysis, where the [111] \(c\) was corresponded to [001] \(_{\text{hex}}\) [61]. The oxygen ions filled at the center of faces of the Bi cubic frame. BiFeO₃ has a perovskite type of structure having ferroelectricity at Bi-site with and at Fe-site magnetism is involved [62–64]. In BiFeO₃, polarization is because of stereo chemically active lone pair of Bi³⁺ ion and magnetization is due to Fe⁴⁺ ion. BiFeO₃ is also known as ferroelectric material having its polarization located along the rhombohedral c-axis due to the dislocation of Bi ions comparative to the FeO₃ octahedral [65,66]. In most recent years, neutron diffraction analysis have elucidated antiferromagnetic ordering with [111] \(_c\) [67]. The magnetic moments of Fe³⁺ associated ferromagnetically along [111] \(_c\) and anti-ferromagnetically are aligned between adjacent (111), which leads to an antiferromagnetic ordering of the G-type structure, as shown in Fig. 3c.

Recently, Ting et al. observed that the lead-free BiFeO₃ material \([0.7-x\text{Bi}_{0.5}\text{FeO}_3\cdot0.3\text{BaTiO}_3\cdot x\text{Mg}_0.3\text{Nb}_0.7\text{O}_3]\) showed a large strain. They found that a low hysteresis (H = 5%) and large strain \((S \approx 0.32%\) and \(d_{33} = 800\) pm/V) was obtained, which are the important factors for high temperature actuators applications [68]. Similarly, Ting et al. proposed that the selected rare-earth elements and transition metal elements dopants on to Bi and Fe-sites significantly enhanced the piezoelectricity of pure BiFeO₃ material. They found that substitution of (Sm, Yb, Ho and Y) at Bi-site successfully suppress the impurities and showed relatively high piezoelectricity \((d_{33} > 40$$\text{pC.N}^{-1}$$)\). So, optimized concentration of rare-earth elements could enhance the piezoelectric performance of pure BiFeO₃ material [69].

The Oxygen octahedral rotation angle plays a very critical structural parameter. Gold-Schmidt in 1926, acknowledged a parameter which was tolerance factor ‘t’ to precisely define the constancy of perovskite structure [70]. It was given as \(t = (r_{Fe} + r_O) / \sqrt{2(r_{Fe} + r_O)}\). Where \(r\) is the respective ionic radius and \(l\) is the octahedral periphery length. If we change value of \(t\) along with a change of Bi³⁺ and Fe³⁺ atomic species, then the crystallographic symmetry is affected and change to monoclinic, tetragonal or orthorhombic in various perovskites [71]. The oxygen octahedral showed a strong effect on crystal field that significantly changed the dipole moments, electronic band structures, production and transportation of photo-generated charge carriers during photocatalytic reaction process [72]. The important factors which directly affect the photoactivity of BiFeO₃ are morphology, particle size, electronic band structure, porosity, surface area, etc.

In recent years, many researches focused on optical properties and electronic structure of BiFeO₃, in order to improve photocatalytic activity. Two kinds of band-gaps for BiFeO₃ have been reported, indirect and direct band-gaps. The reported value for direct band-gap is ranged from 2.2 eV to 2.8 eV and 0.4–1.0 eV for indirect [73–78]. Palai et al. [43] confirmed that the temperature can also affect the band-gap of BiFeO₃. They found that the band-gap of BiFeO₃ was successfully reduced from 2.5 eV to 1.5 eV at 550 °C. Additionally, Niu et al. [79] and Fan et al. [80] suggested that the reduction potential of the valence band and the oxidation level of the conduction band
were at +2.60 and +0.44 V, respectively. Therefore, this uniqueness make more favorable candidate for photocatalysis.

1.1.1. Synthesis approaches for BiFeO3

Single phase perovskite bulk BiFeO3 ceramics is challenging to synthesize. During synthesis process, some unwanted impurity phases such as, Bi25FeO39, Bi2Fe4O9 and Bi2O3 are produced along with pure BiFeO3 [81,82]. In order to eliminate the impurities, nitric acid leaching is used after the calcination of mixed bismuth and iron oxides. The impurities cause leakage which restricts to detailed study of saturated hysteresis loops, particularly in bulk material. The leakage in BiFeO3 material is due to the presence of Fe2+ and oxygen vacancies. However, many physical and chemical methods have been studied for synthesis of pure BiFeO3, but among them wet-chemical technique has appealed a great attention. Typically, the solid-state reaction method has been used to synthesize the perovskite-type oxides [83–86].

Table 1. explained various synthesis methods that have been reported for fabrication of BiFeO3. By comparison from Table 1, it can be concluded that the conventional solid-state method produced some impurities during synthesis process. So, wet-chemical method has widely been used for synthesis of BiFeO3 due to low energy requirement with cheap and easy to control the solution parameters. The wet-chemical method includes hydrothermal, co-precipitation, aerosol-spraying, sol–gel, ultrasound, electrospinning methods [86–94]. Recently, hydrothermal process has been used largely due to its low-temperature synthesis process. The low-temperature technique can prevent the production of unwanted impurities because at higher temperature, it destroys the BiFeO3 pure phase. During hydrothermal process, the size, shape and morphology of BiFeO3 can be controlled [95–97].

It is well-known that the shape, size and morphology can significantly affect on the magnetic, electrical and optical properties. Hou et al. [94] used hydrothermal method to fabricate mesoscale BiFeO3 octahedral particles by using (0.5–12 M) concentration of KOH.

The octahedral particles of BiFeO3 was covered with eight (001)hex crystal faces, as shown in (Fig. 4a and b). They also suggested that the BiFeO3 powder could be achieved through ripening mechanisms and through self-assembly (Fig. 4c). Di et al. [98] found that the various BiFeO3 morphologies can be fabricated with hydrothermal method at the various ions concentrations of Bi3+/Fe3+ (0.025–0.0625 M) in the existence of KOH. Xu et al. [97] reported that the effect of different factors such as, KOH concentration, temperature effect, cooling rate, super saturation and compactedness on BiFeO3.

They found that at 4–14 M concentration of KOH at 140–240 °C, high quality BiFeO3 microcrystalline can be synthesized. Additionally, the quality of crystalline structure can be controlled by decreasing the cooling rate and reducing the super saturation. They also included that by providing the optimized environment during hydrothermal process, BiFeO3 crystal can grow in specified direction with large size and good quality for practical applications.

1.2. Steps for enhancement of photocatalytic efficiency of BiFeO3

1.2.1. Effect of doping

The commercialization of BiFeO3 material is yet not possible, as a photocatalytic oxide technology. It may be due to low photocatalytic performance compared with other commercially available materials [103]. Different steps have been taken to overcome problems which restrict its efficiency and increase the activity of photocatalysis of BiFeO3. The BiFeO3 showed an exceptional photoactivity for degradation of organic pollutants. For the cause of aqueous pollutant degradation, various organic contaminates have been used as model contaminants, such as Rhodamine B (RhB), 4-nitrophenol, methyl orange (MO), methylene blue (MB) and 4-chlorophenol for testing of photocatalyst. Where, photocatalytic performance of photocatalyst mainly depends on several factors such as, surface area, nano-structuring, loading of photocatalyst, initial pollutant concentration, kind of organic pollutant and light source. Doping technique is the best method to introduce impurity into photocatalysts.

Typically, a small quantity of dopant can restrict the recombination rate of photo-generated charge carriers which helps in enhancing the photocatalytic activity of photocatalyst. But the choice of a proper dopant is the key factor. If the amount of dopant exceeds to critical value then it may behave as recombination centers for photo-generated charge carriers, which can reduce the photocatalytic performance. Sarkar...
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<td>Co-precipitation</td>
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<td>600 °C/2h</td>
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<td>Sol-gel</td>
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<td>Ultrasound</td>
<td>Iron Nitrate, Bismuth Nitrate, ethylene glycol</td>
<td>Nanoparticle</td>
<td>–</td>
<td>400 + 500 °C / 0.5 h</td>
<td>Soltani et al. [93]</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>Iron Nitrate, Bismuth Nitrate, ethylene glycol</td>
<td>Nanoparticle</td>
<td>–</td>
<td>400 + 500 °C / 0.5 h</td>
<td>Soltani et al. [94]</td>
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<tr>
<td>Hydrothermal</td>
<td>Iron Nitrate, Bismuth Nitrate, KOH, PEG 200</td>
<td>Wafer-like structure</td>
<td>17.5</td>
<td>&gt;410/210</td>
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<td>Hydrothermal</td>
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<td>Nanocubes</td>
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<td>&gt;420/120</td>
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<td>Hydrothermal</td>
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</tr>
<tr>
<td>Template-assisted 360 °C/6 h</td>
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<td>3D-mesoporous networks</td>
<td>62</td>
<td>&gt;400/4 &gt; 400/5</td>
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<td>Nanoparticle</td>
<td>–</td>
<td>&gt;420/150</td>
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<td>550 for 2h</td>
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<td>400 for 0.5h 500 for 0.5h</td>
<td>Wang et al. [98]</td>
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<td>Nanocomposites</td>
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<td>60 for 10h</td>
<td>Dai et al. [99]</td>
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<td>Solution combustion method</td>
<td>Iron Nitrate, Bismuth Nitrate, Al-Nitrate, Nitric acid</td>
<td>Nanopowder</td>
<td>–</td>
<td>200 for 5 min And, 550 for 3h</td>
<td>Azam et al. [100]</td>
</tr>
<tr>
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<td>Nanopowder</td>
<td>–</td>
<td>650 for 2h</td>
<td>Longu et al. [101]</td>
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<td>Pechini method</td>
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<td>Nanopowder</td>
<td>–</td>
<td>850 for 2h</td>
<td>Garcia et al. [102]</td>
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et al. [104] synthesized nanofibers of Dy-doped BiFeO$_3$ with electrospinning method. The photocatalytic degradation of methylene blue confirmed that DY-doped BiFeO$_3$ nanofiber showed enhanced photocatalytic efficiency under visible-light. It may be due to the fact that Dy modified the band-gap, helped in relocating the charge carriers to the photocatalytic surface, which decrease the rate of recombination of charge carriers. In another report, they found that the doping of Sc onto BiFeO$_3$ can be effective for degradation methylene blue using sunlight. It was observed that the Sc-doped BiFeO$_3$ degraded methylene blue completely within 3 h sunlight irradiation and only 69% of Methylene blue was degraded with pure BiFeO$_3$. It was due to the distortion in BiFeO$_3$ structure after Sc doping that led to improve its ferroelectric properties. After that, researcher started investigations on co-doping onto BiFeO$_3$ with different elements on Bi$^{3+}$ and Fe$^{3+}$-sites [105].

Vanga et al. [106] synthesized Nd and Ni, as co-dopant onto BiFeO$_3$ at Bi$^{3+}$ and Fe$^{3+}$-sites, respectively. They found that the co-doping of Nd and Ni facilitated the charge transfer and decreased the recombination rate of photo-generated charge carriers, which enhanced the photocatalytic performance under visible-light. Irfan et al. [107] synthesized mesoporous BiFeO$_3$ nanostructures with different morphology structures by using double solvent sol-gel method technique. They found that with the co-doping of lanthanum and manganese into Bi$^{3+}$ and Fe$^{4+}$ site of BiFeO$_3$, the surface area was enhanced (3.3–9) m$^2$/g significantly with the large reduction of band-gap (2.08–1.49) eV was observed. The Bi$_{0.93}$La$_{0.07}$Fe$_{0.95}$Mn$_{0.05}$O$_3$ photocatalyst degraded about 97% of Congo red organic pollutant within two-hour visible light irradiation as shown in Fig. 5(a–d). Bharathkumar et al. [108] synthesized BiFeO$_3$ mesh and observed ~98% of the MB dye was degraded within 4 h sunlight irradiation. The improved photocatalytic efficiency was due to the interaction of dye molecules and photocatalyst and bend-bending. This band-bending provided an extra path for transportation of photo-generated charge carriers towards photocatalyst-dye interface region, which reduced the recombination rate of charge carriers, resulting an enhanced photocatalytic performance.

Huo et al. [44] found that BiFeO$_3$ microsphere exhibited eight times more degradation efficiencies for methylene blue, compared to TiO$_2$ (Degussa P25). Moreover, it was observed that the dye molecules in organic dye solution can also absorbed light which make it difficult to define the photoactivity of photocatalyst. Moreover, some colorless organic compounds were also being used to study the photocatalyticities of BiFeO$_3$ such as. Irfan et al. [17] investigated that increasing the charge carriers capturing centers, the photocatalytic activity of BiFeO$_3$ can also enhanced and speed up the photocatalyst activity under different wavelength of lights, because these charge carriers carriers capturing centers increased the recombination time of the carriers, which produced more radicals and hence, increased the activity. They found that the La and Se co-doped BiFeO$_3$ sample (Bi$_{0.95}$La$_{0.05}$Fe$_{0.95}$Se$_{0.05}$O$_3$) degraded the Congo red only in 50 min. It may be due to enlarged surface area (3.3–10) m$^2$/g$^{-1}$, decreasing the recombination time and reduced band-gap (2.06–1.97) eV after co-doping of La and Se onto BiFeO$_3$ as shown in Fig. 6(a–f). The Fig. 7(a–f) confirmed the high crystallinity of pure and co-doped BiFeO$_3$.

In most recent years, researchers have been focused on fabricating BiFeO$_3$-based photocatalyst for not only one region but make it useful for different wavelength of light simultaneously.

1.2.2. **Surface morphology**

Many researches have focused on improving the photocatalytic activity by obtaining the optimum morphology and refining its structure [93,95,109,110]. A solvothermal-assisted method having citric acid as chelating effect was used to fabricated novel BiFeO$_3$ microsphere as a photocatalyst as shown in Fig. 8. The reported material showed higher photocatalytic performance under visible light photocatalysis by degradation of methylene blue as degrading organic pollutant. It may be due to its physicochemical behavior such as crystalite structure, surface area, hollow structure etc. The size of crystal significantly effects on photocatalytic activity due to easily transfer of charges to the surface of photocatalyst and the increased surface caused to provide more surface for incoming photo-generated charge carriers that absorbed more incoming lights (Fig. 8).

Moreover, Huang et al. [111] used microwave hydrothermal method at low temperature (200 $^\circ$C) to synthesize different morphologies of BiFeO$_3$ having surfactant and without surfactant. The morphology of BiFeO$_3$ varied without, with (polyvinylpyrrolidone) and with (ethyleneaminitetraacetic acid) surfactant as ball like, honeycomb-like and flower-like morphologies, respectively. The honey-comb like morphology
showed the highest photocatalytic degradation efficiency for Rhd pollutant, due to its higher surface area (12.38 m²/g) as compared to ball like (7.48 m²/g) and flower like (3.48 m²/g) morphologies. So, surface area could be one of the key factors for improving the photocatalytic activity under light irradiation. Electrospinning method can also be used to synthesized BiFeO₃ nanofibers and found to be an effective photocatalyst by degrading of RhB under visible light. Moreover, the synthesized nanofibers unexpectedly exhibit the super paramagnetic behavior.

Furthermore, a ferromagnetic nature was also observed at room temperature having 4.4 emu/g saturation magnetization and 170 Oe coercivity. Recently, the morphology of BiFeO₃ has been altered to make facets more reactive for photocatalytic process [89,96,112]. Recently, the published reports confirmed that the modification of facet morphology can improve the production of photo-generated charge carriers and slow down the recombination rate which enhanced its photocatalytic activity [111]. Wang et al. synthesized different morphologies of BiFeO₃ with PVF-assisted hydrothermal method using various alkaline conditions. Different kind of morphologies was synthesized such as cube-like particles, spindles-like structures, and plate-like structures with different NaOH concentrations 2 M, 0.5 and 4 M, respectively. Wang et al. studied different crystal structures of BiFeO₃ was with XRD and HRTEM analysis [89].

The BiFeO₃, with plate-like structure exhibits the highest photocatalytic activity by degrading methyl orange under visible light irradiation. It may be due to the fact that the incoming light faced more surface area, more photons were absorbed which generate large number of photo-generated charge carriers that significantly improved the photocatalytic performance of plat-like BiFeO₃ structure. Fei et al. synthesized BiFeO₃ nanoparticles having various largely exposed facets with addition of polyethylene glycol and KOH. The BiFeO₃ rods and pills having (111)c facets exhibit an enhanced photoresponse as compared to {100}c dominant BiFeO₃ cubes [113].

1.2.3. Heterojunctions

Heterojunction, is the overlapping of two band-gaps of different semiconductors, which facilitate the charge carriers in transformation from one level to another with the existence of conducting interface and noble metallic [81,82,111,114,115]. It was due to the creation of Schottky barrier at the heterojunction which inhibited the recombination of charge carriers that improved the photocatalytic activity. Another useful method is the band-gap absorption of plasma absorption from some semiconductors materials which can reduces the band-gap of BiFeO₃. Zhang et al. synthesized Ag and Au nanocomposites by template assisted evaporation method and study the photocatalytic efficiency by degrading RhB [116]. These nanocomposites showed enhanced photocatalytic activity under visible light irradiation. It could be due to superior near field amplitudes of localized surface plasmon of nanoparticle, which decreased its recombination time. Another research group fabricated Pt-BiFeO₃ heterostructure and observed its photodegradation efficiency for methyl

![Image](image_url)

Fig. 5 – (a) UV-vis absorption spectra of pure and La and Mn co-doped BiFeO₃, (where inset is the calculated band-gap value) (b) The photo-degradation efficiencies of CR as a function of irradiation time under visible-light for BLFMO and comparison with pure BFO, (c) FESEM micrograph of well-ordered mesoporous nanostructure of BLFMO-5 (the scale bar in the inset is 1 μm), and (d) N₂ gas isotherms measured at 77 K for BLFMO-5 (where inset represents differential pore size distribution curve from BJH method). [Reproduced with permission, [107].]
Fig. 6 – (a) XRD patterns for pure and La$^{3+}$, Se$^{4+}$ co-doped BiFO$_3$, (b) absorption spectra of BLFSeO samples (where inset represents calculated band-gap), (c) $N_2$ gas isotherms measured at 77 K for BLFSeO-7.5 (where inset represents differential pore size distribution curve from BJH method), (d–f) photocatalytic degradation efficiencies of Congo Red (CR) in the presence of BLFSeO under visible (d), UV (e), and near-infrared (f) irradiation. [Reproduced with permission, [17].]

orange under visible light [79]. The Pt-BiFeO$_3$ heterostructured degraded methyl orange five times more, compared to pure BiFeO$_3$ as shown in Fig. 9(a). This confirmed that the contact of Pt with BiFeO$_3$ was favorable for production of charge carriers and their interaction at photocatalyst interface as shown in Fig. 9(b).

Many researchers studied that many heterojunction photocatalyst such as, SrTiO$_3$/BFO, Fe$_2$O$_3$/BFO, g-C$_3$N$_4$/BFO,
(Na$_{0.5}$Bi$_{0.5}$)TiO$_3$/BFO and CuO/BFO have also improved the photocatalytic performance using visible light [115,117–119]. These results confirmed that the heterostructured materials could be another efficient method for enhancing the photocatalytic performance of BiFeO$_3$.

Production of O$_2$ vacancies: Moreover, another effective method to improve photocatalytic activity is to create oxygen vacancies into BiFeO$_3$ structure. So, by creating critical amount of O$_2$ vacancies, the band-gap of BiFeO$_3$ can also be reduced and it also increases the charge mobility and separation of charges effectively [120,121]. Many researches have already been focused on improving the light absorption capability of BiFeO$_3$ by using various semiconductors oxides such as, BiIO, ZnO, SrTiO$_3$, and TiO$_2$ [122–125]. The similar behavior was also observed for BiFeO$_3$. For example, Wang et al. [126] synthesized BiFeO$_3$ with the presence of oxygen vacancies, by high pressure (2.0 MPa) hydrogenation process. They found that the amount of oxygen vacancies can be controlled by the temperature of hydrogenation, which showed significant effect on photocatalytic performance of BiFeO$_3$. The existence of oxygen vacancies was confirmed by TGA, XPS, DRS, UV–vis and PL analysis. The band-gap was also reduced with increasing oxygen vacancies concentrations and hydrogenated BiFeO$_3$ at temperature 150 °C exhibits three times more enhanced photocatalytic activity compared to pure BiFeO$_3$. Similar results were observed by synthesizing cylinder-like BiFeO$_3$ photocatalysts that efficiently degraded RhB under visible light [127].

The enhanced photocatalytic activity was due its cylinder-like shape and huge amount of oxygen vacancies.

1.2.4. Composites with carbon materials
Another important factor is the carbon materials due to its potential characterization such as thermally stable, resistant to corrosion, large surface area etc. It has already been established that the junction of carbon materials and semiconductor materials can efficiently hinder the recombination of charge carriers, which improve the photoactivity of BiFeO$_3$ [128–131]. For example, Wang et al. [115] synthesized g-C$_3$N$_4$ nano-sheets decorated on BiFeO$_3$ spindle like nanoparticles with deposition precipitation technique and found to be an extraordinary effective photocatalyst for degrading methyl orange for visible light photocatalysis as shown in Fig. 10(a–f). It degraded about (∼75%) of methyl orange pollutant compared to BiFeO$_3$ and g-C$_3$N$_4$. In another report, a research group synthesized BiFeO$_3$-graphene nanocomposites with hydrothermal technique [128] and found it an efficient photocatalyst which degraded congo red under visible photocatalysis. The enhanced coupling between BiFeO$_3$ and graphene was due to the production of Fe–O–C bonds that facilitated with –OH groups which was confirmed by Raman analysis. It may be due to effect of covalent bond and modified band-gap between GO and BiFeO$_3$ and due to p-p stacking process on the surface of graphene which help in large absorption of Congo red.

![Fig. 8 – SEM micrographs of (a) pills, (b) rods and, (c) cubes of BiFeO$_3$. [Reproduced with permission, [113].](image1)

![Fig. 9 – (a) Diffuse reflectance spectra of BiFeO$_3$ and Pt-BiFeO$_3$ (inset is the calculated band-gaps), and (b) basic photo-degradation mechanism of MO. [Reproduced with permission, [79].](image2)
1.2.5. Reusability and structural stability of BiFeO$_3$

The reusability and stability of any photocatalyst is the key factor that determined its practical application. Huo et al. [44] found that the after five cyclic runs, the structure of BiFeO$_3$ microsphere was nearly same and was easily removed from the solution after degradation of RhB under visible light illumination which is shown in Fig. 11(b). Syed et al. [132] investigated that the samarium and manganese co-doped BiFeO$_3$ photocatalysts can be recycled successfully even after four cyclic runs by the degradation of congo red with minor change in the crystal structure as shown in Fig. 11(d). Similarly, the stability of gadolinium and tin co-doped BiFeO$_3$ nanoparticles was also observed by Syed et al. [133] The found that at the optimum doping concentration of Gd$^{3+}$ and Sn$^{4+}$ onto BiFeO$_3$ degraded successfully not only in visible light, but also showed an effective photocatalytic activity under UV and NIR regions of lights.

They also found the Bi$_{0.90}$Gd$_{0.10}$Fe$_{0.95}$Sn$_{0.05}$O$_3$ photocatalyst stable under three different regions and the different types of organic pollutants after four cyclic runs, shown in Fig. 11(f). Papadas et al. [95] found that 3D mesoporous structure of BiFeO$_3$ can be recycled three times which showed its stability. It can easily be recovered from 4-nitrophenol mixture with an external magnet. For practical application, the recovering of BiFeO$_3$ is an important factor. Due to magnetically active property of pure BiFeO$_3$, making it easier to collect from the solution after photocatalytic process. These BiFeO$_3$ sheets can be separated from the solution with using forceps. After all the above discussion, the photocatalyst should thermally stable, less harmful and environment friendly.

1.3. Fabrication and modification of BiFeO$_3$ film

The recyclability of photocatalyst is a key factor for its practical applicability. For this, thin films can be efficiently used repeated without any loss of nanoparticles [131,134,135], 115,122,123] Mahboobeh et al. [136] synthesized forest-like BiFeO$_3$ thin films by electrophoretic deposition technique. They found that the as-synthesized BiFeO$_3$ thin films produced photo-induced electrons, which in result, generates photovoltage and photocurrent. The various concentrations of phenol (15 ppm–80 ppm) organic pollutant were successfully degraded with the forest-like BiFeO$_3$ films within 2 h of visible-light irradiation. Similarly, Hao-min et al. [137] successfully fabricated single-phase polycrystalline BiFeO$_3$ thin films onto F-doped SnO$_2$, (FTO) Pt/Ti/SiO$_2$/Si and Sn-doped In$_2$O$_3$ (ITO) with chemical solution deposition method by chemical solution deposition.

They observed a band-gap tuning from 2.67 eV to 2.02 eV, which helped in enhancement of photocatalytic activity of thin film by degrading Congo red under visible-light. The BiFeO$_3$ film synthesized on Pt/Ti/SiO$_2$/Si substrate showed highest photocatalytic activity during the degradation of Congo red organic dye due to it small grain size. Additionally, weak ferromagnetic behavior was also observed, which probably due to coexistence of Fe$^{2+}$ and Fe$^{3+}$. So, it can be concluding that the BiFeO$_3$ thin films with different substrate can be an effective photocatalyst with better photocatalytic and ferromagnetic properties. In addition, some researchers used photo-Fenton process in order to improve the photocatalytic performance with joining Fenton reagents like H$_2$O$_2$.
with Fe$^{2+}$ ions and create the oxygen species with light irradiation [124–129,138–141].

1.4. Summary and outlook

An effort has been made to discuss recent development of BiFeO$_3$ as photocatalysts, degradation mechanism, synthesis methods, photocatalytic degradation efficiencies of BiFeO$_3$ and their modified structures by degrading different organic pollutants under visible light irradiation. Although considerable development has been accomplished, some important technical issues that needs to be observed further. They are defined as follows: (i) the thin film fabrication of BiFeO$_3$ should be of high photocatalytic activity, (ii) the photo-degradation efficiencies for colorless organic compounds under visible light irradiation, (iii) In-depth study of the mechanism of visible light-responsive BiFeO$_3$ with some computational techniques, (iv) fabrication of various type of porous BiFeO$_3$ and their photocatalytic degradation efficiencies under different wavelength of light. Therefore, considering the above mentioned points, some more exciting results in BiFeO$_3$ photocatalysis could be obtained in the near future.

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Conflicts of interest and authorship conformation form

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