

CHAPTER II

LITERATURE REVIEWS

2.1 $\text{PbBi}_2\text{Nb}_2\text{O}_9$ photocatalyst

$\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Lead Bismuth Niobium Oxide) has a crystal structure that is related to the perovskite structure, belongs to the bismuth oxides family with a structure consisting of perovskite layers ($\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$) between bismuth oxide layers (Bi_2O_2) (Bi, Wu, Li, Wang and Fu, 2008). In this compound, lead (Pb) occupies the A-site, while bismuth (Bi) and niobium (Nb) occupy the B-site as shown in the Figure 2.1. $\text{PbBi}_2\text{Nb}_2\text{O}_9$ is a compound that has been investigated for various applications, including its potential use as a photocatalyst. Its specific properties and potential as a photocatalyst may depend on factors such as its composition and the synthesis method used.

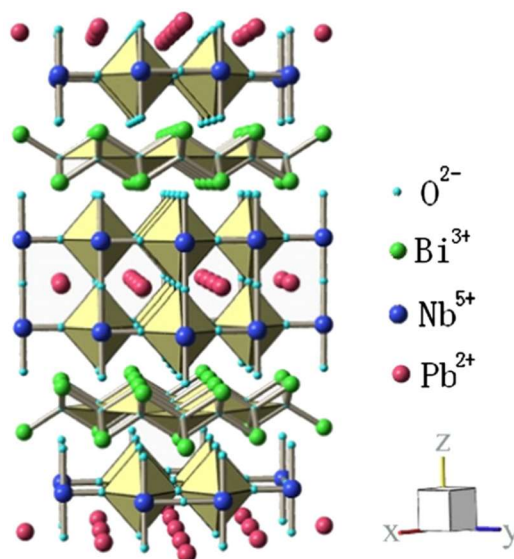


Figure 2.1 Schematic structure of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Bi et al., 2008).

$\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBNO) has a double perovskite structure, which is characterized by its unique crystal arrangement. Double perovskites are a class of materials that have two different cations occupying the B-site of the perovskite structure, rather than a single cation as in the standard perovskite structure. This arrangement results in a crystal structure

that is distinct from the simple perovskite structure, and it can lead to unique properties and behaviors in the material. Double perovskites like $\text{PbBi}_2\text{Nb}_2\text{O}_9$ have been of interest for their potential in various applications, including photocatalysts.

The synthesis method plays a crucial role in determining the specific properties and characteristics of materials like $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Different synthesis methods can yield materials with varying structures, compositions, and properties. In solid-State Reaction (SSR) method (Vijaya Sankar and Ashok, 2020), reactants are mixed in a solid state and heated to initiate chemical reactions that lead to the formation of the desired compound. This method can produce well-crystallized materials but may require high temperatures and long reaction times. Hydrothermal synthesis (HT) (Xie, Chang, Yang, Jiang and Zhao, 2016) involves the use of high-temperature and high-pressure aqueous solutions to promote chemical reactions. This method is known for producing finely crystalline and high-surface-area materials. It can result in materials with different morphologies and surface properties compared to SSR. In molten salt synthesis (MS) (Wendari et al., 2021), reactants are melted in a high-temperature salt medium. This method can lead to materials with unique properties and structures. It is particularly useful for compounds with high melting points. Sol-gel methods (SG) (Wu et al., 2012) involve the formation of a sol (a suspension of nanoscale particles in a liquid) and subsequent gelation to form a solid material. Modified sol-gel methods are variations of the traditional sol-gel process and are often used to tailor the properties of materials, including PBNO, by incorporating dopants or altering reaction conditions.

The study by Wu reports the successful preparation of nanocrystalline PBNO using a modified sol-gel method and its application as a photocatalyst for the reduction of 4-nitroaniline (4-NA) to p-phenylenediamine (PPD). The reduction process achieved a remarkable 99% selectivity and was conducted under visible light irradiation for 150 minutes in a nitrogen (N_2) atmosphere (Wu et al., 2012). The reaction mechanism involved the use of $\text{C}_2\text{O}_4^{2-}$ ions as hole scavengers. In photocatalytic processes, electrons and holes are generated. Hole scavengers help prevent the recombination of electrons and holes, enhancing the efficiency of the photocatalytic reaction. A mechanism for the photocatalytic reduction of 4-NA to PPD in Figure 2.2.

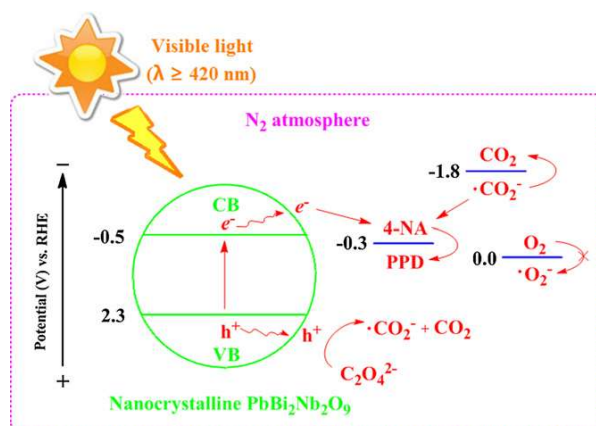


Figure 2.2 Mechanism for the photocatalytic reduction of 4-NA to PPD by nanocrystalline $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Wu et al., 2012).

The study by Sankar and Ashok (Vijaya Sankar et al., 2020) compares the effects of two different preparation methods, solid-state reaction (SSR) and sol-gel (SG), on the properties and performance of PBNO. The study found that PBNO-SG, synthesized via the sol-gel method, exhibited smaller crystalline size and a higher surface area compared to PBNO-SSR, synthesized through solid-state reaction. Smaller crystalline size can lead to more exposed surface area, which is often beneficial for catalytic applications. This provides a larger number of active sites for chemical reactions. PBNO-SG had lower photoluminescence intensity compared to PBNO-SSR. This suggests that PBNO-SG exhibited a lower recombination rate of electron-hole pairs. In photocatalysis, a lower recombination rate is desirable because it means that more charge carriers (electrons and holes) are available for chemical reactions, resulting in more efficient photocatalysis. PBNO-SG was found to be more suitable for degrading organic pollutants under visible light compared to PBNO-SSR.

2.2 Modified $\text{Pb}_2\text{Nb}_2\text{O}_9$ photocatalysts

Modifying the structure and properties of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ through cation substitution is a common strategy researcher to tailor materials to meet specific performance requirements. The choice of the cation and the extent of substitution play crucial roles in determining the final properties of the modified material. These

modifications can have a significant impact on the performance of material in photocatalytic applications. Examples of cation substitutions include W^{6+} (Kim, Borse, Jang, Jeong and Lee, 2008), La^{3+} , Nd^{3+} (Wendari et al., 2021) and Fe^{3+} (Gu, Kim, Kim and Lim, 2023). Each of these cations has unique properties and ionic radii, which can result in various changes to the structure of material and behavior.

The partial substitution of niobium ions (Nb^{5+}) with tungsten ions (W^{6+}) in the PBNO crystal structure was reported by Kim et al. (Kim et al., 2008). It is mentioned that when the tungsten doping in $PbBi_2Nb_{2-x}W_xO_9$ exceeds $x=0.15$, the particles lose their uniformity and more phase impurities appear. This suggests that there may be a limit to the amount of tungsten that can be effectively substituted into the crystal structure without adversely affecting the material's uniformity. Despite the potential limitations in terms of uniformity and phase impurities, the W-doped PBNO material is reported to exhibit high photodecomposition activity.

Fe-doped $PbBi_2Nb_2O_9$ (Gu et al., 2023), denoted as PBFNO, was synthesized through a solid-state reaction method. Iron (Fe) was used as a dopant, and it was incorporated into the crystal structure by substituting Bi ions. The XRD pattern (Figure 2.3) revealed significant changes in the structure of material after Fe doping. The highest peak shifted, and the peaks broadened. This is attributed to a small decrease in the lattice distance, which is a result of substituting the larger ionic radius of Bi^{3+} ($0.96 \text{ \AA}$) with the smaller ionic radius of Fe^{3+} ($0.64 \text{ \AA}$). This structural change can have a profound impact on the material properties.

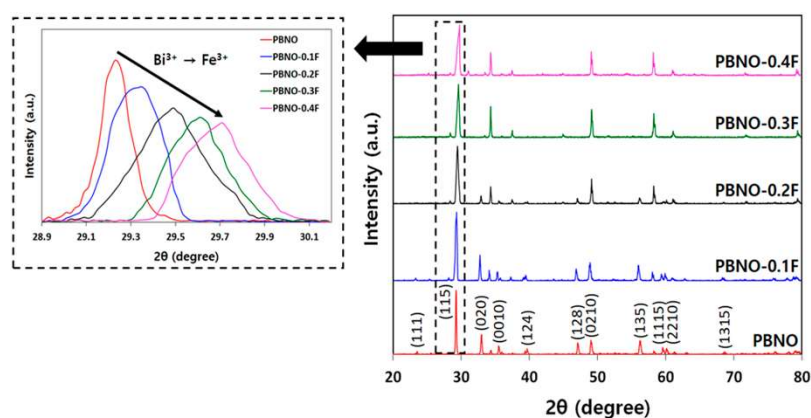


Figure 2.3 XRD patterns of as-prepared PBNO and PBFNO samples by solid-state reaction.

The band gap energy of PBFNO was found to decrease compared to the pristine PBNO. This suggests that PBFNO is better suited for absorbing and utilizing visible light energy for photocatalytic reactions. The presence of Fe dopants in PBFNO is reported to have a dual role. Firstly, they form intermediate bands, which can facilitate absorption of photons at specific energies. Secondly, they serve as electron-hole traps, which reduce the recombination of charge carriers. The reduction in photoluminescence intensity after Fe doping suggests that fewer charge carriers are recombining, enhancing the material's charge separation efficiency. Interestingly, the statement also mentions that the excess Fe dopants act as recombination centers. These are locations where electrons and holes recombine, potentially reducing charge separation efficiency. However, despite this, PBFNO demonstrates superior photocatalytic activity for the degradation of methylene blue, particularly under visible light irradiation at pH 12.

2.3 Modified photocatalyst by Ce-doping

Cerium is indeed an interesting element among the lanthanides due to its unique properties, including its band gap, optical properties, and catalytic potential. A smaller band gap, indicates that cerium can efficiently absorb light in the visible region, making it a good candidate for various optical applications. Absolutely, the ability of cerium to transition between Ce^{3+} and Ce^{4+} oxidation states enhance its catalytic potential (Ellappan and Miranda, 2014).

The cerium is doped into titanium dioxide (Chen et al., 2010) (Liu, Li, Leng and Li, 2003), it results in a shift towards the visible region in terms of its optical properties. This shift towards the visible region can make the material more effective in capturing and utilizing visible light, which has important implications for applications such as photocatalysis and solar energy conversion.

The role of Ce-doped TiO_2 in photocatalysis (Cerrato, Gaggero, Calza and Paganini, 2022). Ce ions can exist in two oxidation states, Ce^{3+} and Ce^{4+} . The presence of these ions can serve as electron traps, which means they can capture and store electrons, reducing the recombination of electrons and holes. This is a critical factor in enhancing the efficiency of photocatalytic reactions. Ce-doping can also extend the

absorption range of TiO_2 into the visible light spectrum. Moreover, the introduction of Ce ions into TiO_2 can create additional catalytic active sites on the surface of the photocatalyst. These active sites facilitate the interaction between the photocatalyst and the target molecules in the photodegradation reaction, such as organic pollutants like methyl orange. The mechanism of methyl orange degradation as shown in Figure 2.4.

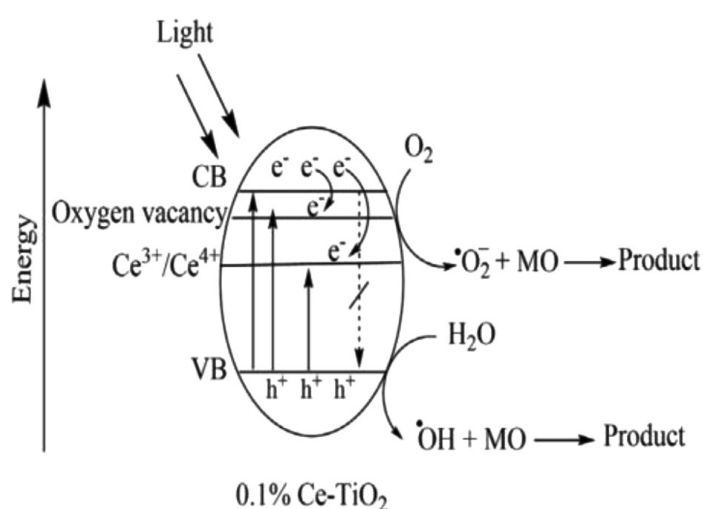


Figure 2.4 The mechanism of methyl orange dye degradation over 0.1% Ce-doped TiO_2 under UV light irradiation.

Photocatalytic hydrogen evolution study the behavior of hybrid $\text{Ce}^{4+/3+}$ doped into perovskite magnesium zirconate nano cubes (MgZrO_3 NCs) (Prashanth et al., 2021) to methyl orange degradation. The band edge positions in pristine ZrO_2 and MgZrO_3 are shown in the Figure 2.5, Incorporation of Ce dopant to MgZrO_3 modified the band edge positions of $\text{Ce}^{4+/3+}$: MgZrO_3 NCs. The shift in band edge positions indicated that the introduction of Ce dopants led to an increase in the generation of electron-hole pairs upon exposure to light. The rearrangement of band edge positions and the greater electro positivity of zirconia in $\text{Ce}^{4+/3+}$: MgZrO_3 NCs played a role in suppressing the recombination of photo-generated electrons and holes.

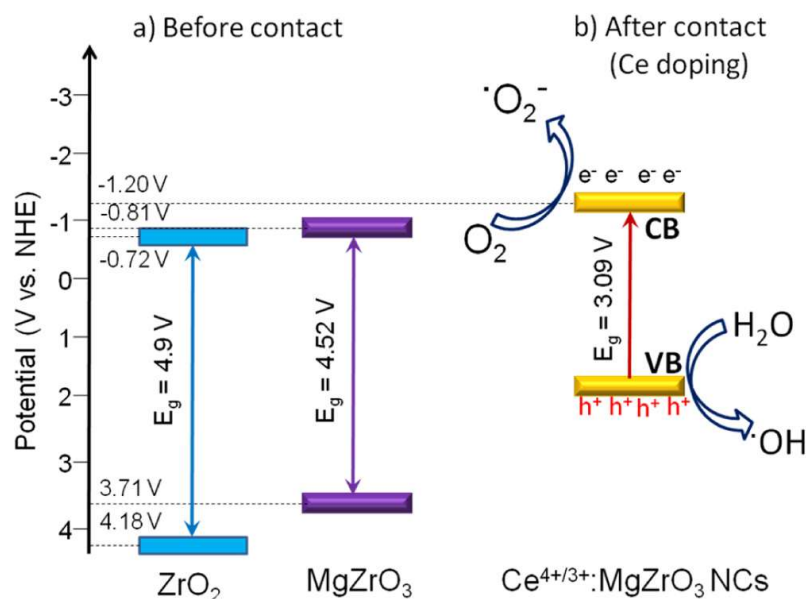


Figure 2.5 Band edge positions of (a) Pristine ZrO_2 and MgZrO_3 (b) Band alignment in case of $\text{Ce}^{4+/3+}:\text{MgZrO}_3$ NCs.

As a result of the modified band edge positions and the suppression of recombination, the $\text{Ce}^{4+/3+}:\text{MgZrO}_3$ NCs, containing 9 mol% of Ce dopant, exhibited a significantly higher photocatalytic activity. They achieved a photocatalytic hydrogen production rate of $13,318 \mu\text{mol h}^{-1}\text{g}^{-1}$, which was 6.2 times greater than pristine ZrO_2 and 4.1 times greater than MgZrO_3 . This suggests that the introduction of Ce dopants enhanced the efficiency of hydrogen generation. In addition, methyl orange degradation efficiency of $\text{Ce}^{4+/3+}:\text{MgZrO}_3$ NCs reached 93% within 120 minutes. This high efficiency can be attributed to the presence of abundant photo-active centers and defects within the material, which again helps in suppressing charge carrier recombination and promotes efficient dye degradation.

The study by Cao investigates the use of Ce-doped BiFeO_3 (BCFO) as a photocatalyst to enhance the photo-Fenton degradation of tetracycline (TC). In the photo-Fenton system, the researchers utilize a combination of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) activated by light to generate hydroxyl radicals ($\cdot\text{OH}$) (Cao et al., 2024). A previous study by Lu revealed that pure BiFeO_3 (BFO) had a high electron-hole recombination rate. This recombination can reduce the efficiency of the photocatalytic process. Ce^{3+} ions, introduced into the BCFO structure, have the

capability to activate H_2O_2 and $\cdot\text{OH}$, similar to Fe^{2+} (Lu et al., 2022). This makes Ce^{3+} ions valuable for enhancing the photo-Fenton reaction. Meanwhile, cerium is doped into the BFO structure as Ce^{4+} , which has a higher valence than the original Bi^{3+} ions. This Ce^{4+} can act as a donor ion within the oxygen octahedron, helping to maintain charge neutrality and suppress the formation of oxygen vacancies (OVs) in the material. The introduction of Ce ions into BFO narrows the band gap of the material. The photoluminescence intensity of BCFOs is lower than that of BFO, indicating a reduction in the electron-hole recombination rate. While Ce doping has beneficial effects on photocatalytic performance, the study found that when the Ce content was increased to 9%, excess Ce prevented H_2O_2 from decomposing effectively. It also precipitated out and formed cerium dioxide (CeO_2), which coated the active catalytic sites and acted as a recombination center for photogenerated carriers. As a result, the researchers found that 7% Ce doping provided the best photocatalytic performance. The photo-Fenton system using BCFO-7 as a photocatalyst achieved a high degradation rate of tetracycline (TC), reaching 97% at an initial pH of 3, and maintaining a degradation rate of 91% at pH 4. The mechanism for the degradation of TC by BCFO-7 is shown in the figure 2.6.

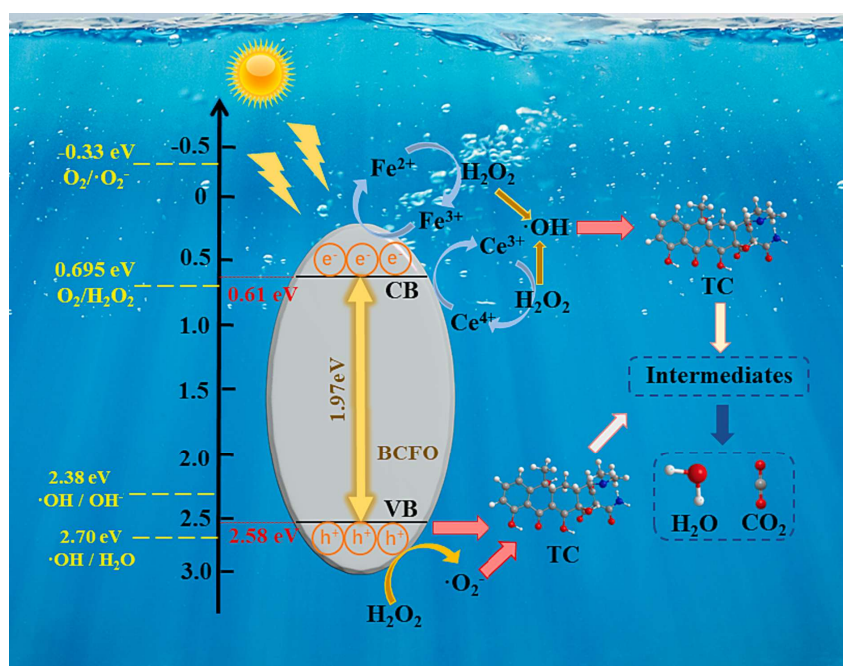


Figure 2.6 Mechanistic diagram of TC degradation by BCFO-7.

2.4 References

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