Perovskite Oxide–Based Materials for Photocatalytic and Photoelectrocatalytic Treatment of Water

Oluchi V. Nkwachukwu1 and Omotayo A. Arotiba1,2*

1Department of Chemical Sciences, University of Johannesburg, Johannesburg, South Africa, 2Centre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, South Africa

Meeting the global challenge of water availability necessitates diversification from traditional water treatment methods to other complementary methods, such as photocatalysis and photoelectrocatalysis (PEC), for a more robust solution. Materials play very important roles in the development of these newer methods. Thus, the quest and applications of a myriad of materials are ongoing areas of water research. Perovskite and perovskite-related materials, which have been largely explored in the energy sectors, are potential materials in water treatment technologies. In this review, attention is paid to the recent progress in the application of perovskite materials in photocatalytic and photoelectrocatalytic degradation of organic pollutants in water. Water treatment applications of lanthanum, ferrite, titanate, and tantalum (and others)-based perovskites are discussed. The chemical nature and different synthetic routes of perovskites or perovskite composites are presented as fundamental to applications.

Keywords: perovskites, water treatment, photocatalysis, photoelectrocatalysis, degradation

INTRODUCTION

A perovskite by definition is a material with the same crystal structure as CaTiO3, BaTiO3, CaSiO3, or SrTiO3. Perovskite mineral was discovered in the Ural Mountains, Russia, in 1839. A German mineralogist and crystallographer named Gustav Rose received the samples from Alexander Kämmerer—a Russian mineralogist. Rose did a lot of work on the determination of the properties of perovskite, and taking that into account, he named this mineral after Lev Perovski, who was a Russian politician and mineralogist (Park et al., 2016; Katz, 2020; Etgar, 2016). Typically, perovskites are binary metal oxides with a general formula ABO3, where A cation can be lanthanide, alkaline, or alkaline earth metal element, and B cation is a metallic element with 3-, 4-, or 5-day configuration (Arandiyan et al., 2018). Perovskite and perovskite-related materials have emerged as an important new class of materials due to their fascinating physicochemical properties such as thermal stability, electron mobility, and redox behavior (Zhu et al., 2015; Arandiyan et al., 2018), and their versatile applications in catalysis, water splitting, solar cells, optical devices, and superconductors (Khalesi et al., 2008a; Khalesi et al., 2008b).

An ideal perovskite structure has an ABO3 stoichiometry and a cubic crystal structure (Figure 1). The cubic cell is composed of a three-dimensional framework of corner-sharing BO6 octahedra. The B-site cation is a transition metal element (Kubacka et al., 2012). The A-site cation occupies the 12 coordinate position formed by the BO6 network and often consists of an alkaline earth metal element...
perovskite ABX₃, perovskite-related structures arise from the loss of one or more of the symmetry operator in the cubic structure and exhibit lattice distortion to varying degrees, thereby resulting in a nonideal structure of the crystal phases such as orthorhombic, rhombohedral, monoclinic, and triclinic phases. Although primitive cubic is the idealized structure, the differences in radii between both cations can in fact distort the structure. This normally involves tilting of the BO₆ units (octahedral tilting; Kong et al., 2019). This distortion is created in the crystalline structure as perovskites adopt a wide range of different composition by partially substituting either A or B cation of the same or different valences, resulting in a general formula A₁-xAₓB¹-yBᵧO₃₋ₓδ, where “+” denotes oxygen excess and “−” denotes oxygen deficiency. It is important to note that both A and B or either offers great flexibility with regard to tailoring and tuning of the physicochemical properties (Zhang et al., 1990; Zhu et al., 2015; Torregrosa-Rivero et al., 2017; Arandiyan et al., 2018). For example, Gade et al. (2018) studied the photocatalytic efficiency in ALaTi₂O₆, where A is Na, Ag, or Cu. This new class of material efficiently and effectively mineralized the Congo red dye, 4-chlorophenol, and 4-4′-bis (2-sulfostyryl) biphenyl used as model pollutants (Gade et al., 2018). The stability of the perovskite is summarized by the Goldschmidt tolerance factor, t = (rA + rO)/ √2 (rB + rO), where rA, rB, and rO are the, respective, radii of A, B, and oxygen ions. For the perovskite structure, the Goldschmidt tolerance factor lies between 0.76 and 1.13 (Zhu A. et al., 2014; Acharya et al., 2015; Kumar et al., 2019).

The diverse composition of emerging pollutants in water suggests that no single method of water treatment can be termed universal. This necessitates the exploration of newer water treatment methods and the tailoring of these methods to certain segments of wastewater. In response to this water treatment challenge, advanced oxidation processes (AOPs) have been developed as an effective technology to remove persistent organic pollutants from wastewater. AOPs are based on in situ generation of radicals that nonselectively react with most organics and are able to degrade highly recalcitrant compounds (Brillas and Martinez-Huitle, 2015; Garcia-Segura and Brillas, 2017; Peleyeju and Arotiba, 2018; Umukoro et al., 2018). This review is in addition to the existing body of knowledge around AOPs for water treatment. It is however distinct as it focuses on the application of perovskites in advanced oxidation processes related to water treatment. The so-called first-generation photocatalysts such as TiO₂, SnO₂, and ZnO have the limitations of wide bandgap and thus only UV responsive. The second-generation photocatalysts (WO₃, Fe₂O₃, and Cu₂O) have the challenge of low quantum yield due to their rapid electron–hole recombination and poor stability (Kong et al., 2019). Perovskite and perovskite-related materials are considered as third-generation photocatalysts which form a stable structure and solid solution with several ranges of metal ions to achieve the appropriate band engineering for photoelectrocatalytic applications (Yang et al., 2009; Kong et al., 2019). Emphasis will be on photocatalysis and electrochemically advanced oxidation systems such as electrocatalysis and photoelectrocatalysis, with perovskites as the semiconductor. Prior to the discussions of the applications of the perovskites in water treatment, brief accounts on synthesis and types of this interesting material are provided.

### GENERAL SYNTHESIS METHODS FOR PEROVSKITES

Perovskites are usually formed at elevated temperature because from their composition, perovskite oxides are compounds consisting of two or more simple oxides having high melting points (Arandiyan et al., 2018). The approach to synthesize perovskite oxide must be selected according to the specific application, specific demands of activity, and selectivity as these depend on the arrangement of atoms within its surface (Lim et al., 2019). For example, the solid-state synthesis method is commonly used to prepare perovskite in the pure form due to the availability of impurity-free precursors, and they find application in electronics. The downside of the solid-state synthesis approach is that it requires annealing at high temperature for a long time and frequent intermediary grindings which results in poor homogeneity as well as difficulty in controlling the particle size. Thus, problem arises when perovskites from solid-state methods are subjected to surface-related studies.

Since this review focuses on photocatalysis and photoelectrocatalysis, the methods discussed are those related to improved porosity, to achieve high surface area, etc. Efforts have been made by researchers in synthesizing perovskites at low temperatures with improved porosity (Labhasetwar et al., 2015). To overcome the homogeneity drawback of solid-state methods and to achieve nanocrystalline phase, reproducibility, and pure powder, several groups have focused on wet chemistry methods such as citrate sol–gel method, precipitation method, electrospinning technique, ultrasonic method, hydrothermal method, and microwave-assisted synthesis methods. Wet
chemistry methods are characterized by their simplicity, reduced sintering time, mass production, high level of repeatability, lower temperature (than solid-state reaction), better flexibility in thin film–forming superior homogeneity, improved control of stoichiometry, purity, particle size, and a low industrialization implementation cost (Assirey, 2019). One of the challenges faced in the development of perovskite catalyst is obtaining the right structure and maintaining high surface area because of high calcination temperature employed sometimes during synthesis (Akinlolu et al., 2019). Hence, the choice of method of preparation is a top priority.

**Hydrothermal Method**

The hydrothermal method is a useful technique for synthesizing perovskites. This method depends on solubility of minerals in hot water under high pressure, and many syntheses of perovskites for catalytic purpose have been carried out with various advancements using this method. The hydrothermal method is useful in perovskite synthesis as the particle size and shape can be affected by controlling the reaction temperature, pH, time, and concentration of reactants. Biasotto et al. (2011) hydrothermally synthesized bismuth ferrite (BFO) nanoparticles at a low temperature of 180°C within 1 h. In comparison with solid-state reaction process, the authors recorded submicron crystallites of BFO with enhanced homogeneity. Met and group (Kostyukhin et al., 2019) synthesized LaFeO₃ via a hydrothermal microwave-assisted synthesis at a relatively low temperature of 240°C and pressure of 60 bar. In the procedure, the precursors were mixed in deionized water with the addition of KOH gradually while stirring. The presence of microwave as the heating source assisted in an enhanced crystallization rate of nanoparticles. Gao et al. (2015) synthesized BiFeO₃ using nitrates of bismuth and iron via a hydrothermal method. KOH was added as a mineralizer to assist in the coprecipitation of Bi³⁺ and Fe³⁺. The XRD result shows that a single-phase cube-like BiFeO₃ was successfully synthesized. Also, the effects of reaction time, KOH concentration, and organic dispersant on the BiFeO₃ particle morphology size were investigated. The prepared photocatalyst showed excellent photodegradation of methyl orange dye (MO) under visible light (>420 nm).

Additionally, hydrothermal method has also been adopted for the preparation of doped perovskites as well as perovskite-based heterojunctions. For instance, Baeissia, 2016 synthesized gold-doped NaNbO₃ through a hydrothermal method for photocatalytic degradation of malachite green dye. The morphology of sodium niobate was studied by changing the hydrothermal temperature from 100 to 250°C. The XRD results reveal that all samples prepared at different temperature were of the perovskite structure. The hydrothermal temperature played an important role in the structure and surface area of the obtained sodium niobate as the temperatures at 100, 150, 200, and 250°C led to photocatalysts with surface area of 7, 9, 13, and 16 m²/g, respectively. Wen et al. (2017) synthesized a novel SrTiO₃/BiOI heterostructure photocatalyst through hydrothermal and facile chemical bath methods with the aid of ethylene glycol. The XRD pattern of SrTiO₃ depicts a characteristic tetragonal structure with a cubic SrTiO₃ perovskite structure, and the morphology of SrTiO₃ possesses nanosheets of irregular edges. It was also noticed that the SrTiO₃ nanosheets fasten on the surface of BiOI nanoparticles, forming a SrTiO₃/BiOI. Photocatalytic activity, photoluminescence, and electrochemical impedance spectroscopy analysis confirmed higher photo-induced charge separation efficiency possessed in SrTiO₃/BiOI composites, which they attributed to an intimate contact between SrTiO₃ and BiOI.

These reports show that hydrothermal synthesis is ideal for the preparation of pristine perovskites as well as composites containing perovskites. However, the efficiency of the hydrothermal method is dependent on various modifications of experimental conditions such as temperature and solvents used in dissolution of precursor reagents. Remya and group (Remya et al., 2020) synthesized BiFeO₃ via hydrothermal methods with different experimental conditions for the fine-tuning of the final product (Figure 2).

**Citrate Sol–Gel Method**

The citrate sol–gel method is usually used to prepare nanosized materials. Although its application is limited due to stability of its precursor system, it is difficult to control the chemical composition of complex oxides. The sol–gel procedure in aqueous medium uses inorganic salts and a chelating agent of carboxylic acid such as citric acid as a precursor. This technique has widely been used in making thin films with low temperature. Chu et al. (2018) reported a B site–deficient perovskite prepared via the classic sol–gel calcination method. In these methods, the nitrates of the metal ions were dissolved in deionized water, citric acid, and ethylene glycol to form a homogeneous solution at a certain pH, calcination temperature, and time. The XRD pattern showed that pure perovskite was successfully formed. SEM images revealed that most of the nanoparticles are non-agglomerated due to low calcination temperature. The prepared photocatalyst displayed a good photocatalytic property.

![Figure 2](Image)
In another report, LaMg\textsubscript{x}Fe\textsubscript{3-x}O\textsubscript{3-δ} perovskite prepared via sol–gel route showed a formation of well-crystallized perovskite. LaMgFe\textsubscript{3} and LaMgFe\textsubscript{4} photocatalysts presented a particle size of around 100–150 nm with a well-defined size. The photocatalytic efficiency of LaMgFe\textsubscript{4} was higher than that of other prepared catalysts owing to its smaller particle size distribution and higher surface area (Teresita et al., 2016). Zhang Y. et al. (2019) prepared SrFe\textsubscript{x}Ni\textsubscript{1-x}O\textsubscript{3-δ} (\textit{x} = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) via the citrate sol–gel method (\textbf{Figure 3}). They recorded their optimum catalyst with good electrocatalytic performance for water treatment was prepared at a reaction time of 120 min, a calcination temperature of 700°C, and Fe-doping content of \textit{x} = 0.3.

\textbf{Coprecipitation Method}

Coprecipitation occurs as a result of different cations in solution precipitating simultaneously, and this method encourages homogeneity of products. Coprecipitation plays a critical role in controlling the temperature, concentration, pH, and solution homogeneity. Haron et al. (2017) prepared a nanostructured perovskite oxide such as LaMO\textsubscript{3} (M = Al, Co, or Fe) by the coprecipitation method. They observed a formation of single-phase nanocrystalline with high purity, larger surface areas, and porosity.

Djoudi reported a study on LaAl\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3-δ} prepared via the coprecipitation method using NaOH. They observed an increase in peak shift as the concentration of doping material increases, and crystallinity of all samples varies as the calcination temperature was adjusted. Therefore, the pure perovskite phase sample was calcined at 700°C for 6 h with no impurity. The morphology of the sample showed partial agglomeration, and interestingly, the material exhibited great electroactivity properties, which indicates a good electrocatalyst for oxygen reduction and evolution (Djoudi and Omari, 2015).

\textbf{PEROVSKITE OXIDE–BASED MATERIALS IN PHOTOCATALYSIS AND PHOTOELECTROCATALYSIS}

\textbf{Perovskite Materials in Photocatalysis}

In recent years, advanced oxidation processes (AOPs) have emerged to be efficient and effective methods for the treatment of wastewaters. They are utilized for the removal of organic pollutants during water treatment due to the generation and use of hydroxyl radicals as oxidizing species, which initiate other reactions for the degradation and possibly mineralization of organic pollutants. Among the AOPs, photocatalysis has...
attracted attention as a promising technique for solving environmental problems. Photocatalysis is a process that occurs when a semiconductor absorbs a photon of energy greater than its bandgap (the region between the electron-fill valence band and the empty conduction band of a semiconductor), and an electron is excited to the conduction band, thereby creating a hole in the valence band. The generation of the electrons could lead to oxidation and reduction reactions on the surface of the semiconductor (Umukoro et al., 2016). Semiconductors such as TiO2, SnO, and ZnO are widely used as a catalyst in photocatalytic reactions. TiO2 has been widely applied in photocatalysis owing to its stability, low toxicity, low cost, and high oxidation efficiency. However, its rapid recombination of photogenerated electron–hole pairs and low absorption of visible light are shortcomings that necessitate the need for other materials that have narrower bandgap and wider range of wavelength of light absorption in the visible range, and high solar energy. A suitable photocatalyst should have the following characteristics: i) it should have a bandgap ≥1.2 eV to provide energetic electrons and a bandgap ≤3.0 eV to allow effective absorption of overlap with the solar spectrum; ii) its photogenerated charge carriers should be easily available for use with the electrolyte, and it should be resistant to photocorrosion (Ge et al., 2016; Kumar A. et al., 2020). Other beneficial factors include low cost, facile preparation method, and amenability to bandgap tuning. Perovskites fit into these characteristics to a large extent. The shortcomings of recombination and photocorrosion can be minimized by perovskite composites such as in doping and/or heterojunction formation. Table 1 shows some recent perovskites that found their application on photocatalysis for water treatment. The different classes of perovskites used in PC are discussed in the following sections.

**Lanthanum-Based Perovskites in Photocatalysis**

Lanthanum-based perovskites have raised interest as a result of their intriguing properties such as oxygen mobility, ionic conductivity, and excellent magnetic properties. For example, LaFeO3 had been proposed to be a significant material in photocatalytic areas because it exhibited several attention due to its properties such as narrow bandgap (Eg = 1.86–2.36 eV), more stability, and also environmental friendliness (Yahya et al., 2019). Thus, various synthesis approaches such as using template reagent and doping with other metals have been used to improve surface areas and enhance the charge transfer and light captivation through local surface plasmon resonance to improve its catalytic performance. For instance, Wang and group (Zhang W. et al., 2019) synthesized porous lanthanum–titanium La2Ti2O7 using CTAB as a template reagent through the sol–gel method toward the degradation of azophloxine dye. The authors observed that the presence of CTAB influenced the specific surface area and the crystallinity of the La2Ti2O7. The maximum number of hydroxyl radical was generated on the La2Ti2O7 sample obtained with 4 g of CTAB, which degraded about 100% of the dye after 180 min from UV-Vis absorption analysis. The photocatalytic degradation efficiencies for the first and the fifth cycles are 100 and 91%, respectively. The authors attributed this slight decline to the loss of fine La2Ti2O7 powder when taking solution samples for examination. This observation is consistent with one of the major challenges of photocatalysis—catalyst recovery. Also, in order to improve the photocatalytic performance of lanthanum-based perovskites, multiple complex or layered perovskite oxides containing lanthanum have been used. For example, Verduzco et al. (2018) synthesized a layered perovskite oxide Sr2.7xCa0.3x Ln0.3Fe2O7–δ (Ln = Nd and La) by a conventional solid-state reaction for degradation of methylene blue (MB) dye under solar and UV irradiation.

Varying the stoichiometry or doping of perovskite with a cation of different valence states can change the electronic structure, which dictates the electrical and optical properties (Zhang et al., 2010). The photocatalytic properties of Sr3.2–xCa xLa0.8Fe1.5Co1.5O10–δ (Oliva et al., 2017) were studied by monitoring the degradation of methylene blue (MB) dye. This Ca-doped layered perovskite belonging to Ruddlesden–Popper (R–P) family exhibited increase in absorbance due to the creation of defects such as atomic dislocation induced by the replacement of Sr by Ca. It is worthy to note that the formation of these defects such as oxygen vacancies or trapping centers is suitable for photocatalysis because these oxygen vacancies diminish the rate of electron–hole recombination (Wu et al., 2016). As reported by Oliva et al. (2017), higher photocatalytic degradation was observed as the Ca content increased. The layered perovskites (SCLFCO sample) with x = 0.8 produced a total degradation of MB (100%) after 150 min at a pH = 6.0, whereas the undoped sample with x = 0 showed only a maximum degradation of 27% after 300 min. The authors attributed this to the lower bandgap, the low level of agglomeration, and particle size. The authors also explained that the chemical reaction for the degradation was due to the presence of Cl− ion in MB molecule that balanced the charge with methyl group attached to a positive N+. So the presence of Ca2+ ion on the surface of the doped SCLFCO attracted Cl− in the MB, thereby creating an unbalanced charge that facilitated the breaking of chemical bonds of the methyl groups attached to the chain of the MB molecule. Yang’s group (Guan et al., 2020) immobilized LaFeO2 and Au nanoparticles on the Cu2O surface as a ternary composite photocatalyst for rhodamine B degradation. The composite demonstrated a far more photocatalytic degradation performance than bare LaFeO2 and Cu2O. This avenue assists in facilitating the spatial separation of photo-induced electron hole. In another study, Ag nanoparticle was used to decorate LaTiO3 for the degradation of pesticide in water. The authors (Shawky et al., 2020) observed an improvement in the surface texture as observed from the morphological analysis. The composite demonstrated an enhancement in light absorption and reduced recombination rate as compared to the pure LaTiO3; as a result, complete degradation of atrazine pollutant within 40 min of irradiation was observed. Numerous reports have shown that incorporation or decoration of lanthanum-based perovskites with other metals or semiconductors results in
pronounced enhancement in the photocatalysis (Arabi et al., 2018; Yahya et al., 2019; Chen C. et al., 2020; Nakhostin Panahi et al., 2020).

**TABLE 1** | Recent perovskites in photocatalysis for water treatment.

| Perovskite Co-catalyst | Light source | Method | Pollutant | Pollutant conc | Catalyst conc | Time | % Removal | References |
|------------------------|--------------|--------|-----------|---------------|---------------|------|-----------|------------|
| BiFeO₃ | N-rGO | Hg arc lamp | — | Rhodamine B | 100 mg/L | 10 mg/L | 3 h | 98.7 | Dixit et al. (2020) |
| LaTiO₃ | Ag | 300 W Xe | Hydrothermal | Atrazine | — | 1.2 g/L | 40 min | 100 | Shawky et al. (2020) |
| SrTiO₃ | rGO | 450 W Xe | Hydrothermal | Rhodamine B | 0.04 mg | 0.01 g | — | 94.5 | Rosy and Kalpana (2018) |
| LaMnO₃ | Ca | 25 mg/cm² | Hydrothermal | Methylene blue | 7 ppm | 0.07 g/L | 360 min | 73 | Arabi et al. (2018) |
| CaSnO₃ | rGO | UV | Microwave irradiation | Methylene blue | 10 mg/L | 0.1 g | 150 min | 92 | Venkatesh et al. (2020b) |
| La₄MnTiO₆ | — | 400 W | Sol gel | AB 113 | 50 mg/L | 30 mg/L | 120 min | 72 | Shirazi et al. (2020) |
| SrFeO₃ | CuO | 300 W | Sol gel | Rhodamine B | 20 mg/L | 0.15 g | 120 min | 93 85 | Behzadifard et al. (2018) |
| BiFeO₃ | BiO | — | Hydrothermal | — | 60 ppm | 0.12 g/L | 136 min | — | Bahmani et al. (2020) |
| SrTiO₃ | Ag/Ag₃PO₄ | 500 W Xe | Ball milling | Tetracycline | 0.04 mg | 0.01 g | 94.5 | Rosy and Kalpana (2018) |
| SrTiO₃ | La, Fe | 150 W | Ball milling | Methyl orange | 7 ppm | 0.07 g/L | 360 min | 72 | Arabi et al. (2018) |
| SrTiO₃ | La, Cr | 300 W | Xe | Hydrothermal | Tetracycline | 20 mg/L | 50 mg | 90 min | 83 | Jiang et al. (2019) |
| LaNiO₃ | TiO₂ | 300 W | Xe | Hydrothermal | Tetracycline | 10 mg | 0.2 g/L | 15 min | 72 | Yu et al. (2020) |
| SrZrO₃ | Sb₂O₃ | 450 W | Solid state | Tetracycline | 10 mg/L | 100 mg | 150 min | 100 54 | Chen C. et al. (2020) |
| [NaBi]₂TiO₅ | — | 300 W | Solid state | Methylene blue | 10 mg/L | 1 g/L | 80 min | 92.4 | Xiao et al. (2020) |
| TiO₂ | Nb | 100 W | Gel combination | Methylene blue | 10 mg/L | 15 mg | 120 min | 65 | Haruna et al. (2020) |
| CaTiO₃ | Li | 11 W UV | Solvothermal | Methyl orange | 1 × 10⁻⁴ M | 10 mg | 36 h | N/A | Dong et al. (2020) |
| KTaO₃ | N | 150 W | Solvothermal | Methylene blue | 1 × 10⁻⁵ M | 20 mg | 360 min | Complete degradation | Rao et al. (2018) |
| MgTiO₃ | MgFe₂O₄ | UV | Sol gel | Acid black | 500 ppm | 0.1 g | 30 min | 67.9 | Kiani et al. (2019) |
| CaTiO₃ | Li, Ce | UV | Sol gel | Methylene blue | 20 mg/L | 150 mg | 120 min | 55 | Zhang et al. (2020) |
| BiFeO₃ | Li | 100 W | Sol gel | Methylene blue | 10 mg/L | 50 mg | 90 min | 90.7 | Huerta-Flores et al. (2018) |
| SrSnO₃ | ZrO₂ | UV | Pechni method | Methylene blue | 10 mg/L | 50 mg | 90 min | 90.7 | Huerta-Flores et al. (2018) |
| La₂Ti₂O₇ | CTAB | UV | Sol gel | Methylene blue | 10 mg/L | 50 mg | 90 min | 90.7 | Huerta-Flores et al. (2018) |
| LaFeO₃ | Au, CuO | 200 W Xe | Chemical route | Methylene blue | 10 mg/L | 50 mg | 90 min | 90.7 | Huerta-Flores et al. (2018) |
| LaMnO₃ | CTAB | — | Hydrothermal | Methylene blue | 15 ppm | 5 mg | 315 min | 95 | Priyatharshni et al. (2020) |

Non–Lanthanum-Based Perovskites

The applications of other non–lanthanum-based perovskites in photocatalysis have been reported. The following sections discuss...
ferrite-based, titanate-based, tantalum, and other types of perovskites for photocatalysis.

**Ferrite-Based Perovskites in Photocatalysis**

Iron-based perovskites have the general formula AFeO₃, where A is a metal ion like Ca, Sr, Ba, Bi, La, Gd, Ga, or Y (Tang et al., 2011; Dhanasekaran and Gupta, 2012; Ramadan et al., 2013). Iron-based compounds could also adopt the FeAO₃ structure, where A could be Ti (Gross-Sorokin et al., 2006; AlSalka et al., 2019). In this case, physical properties such as magnetism and/or ferroelectricity, which can be beneficial for the photocatalytic activity, are added to the material. Magnetism and/or ferroelectricity facilitate in extracting the photocatalyst from solution by an external magnet and also assist in the separation of the photogenerated charges.

Ferrite-based perovskites have proven to be promising materials for photocatalytic and photoelectrocatalytic applications in the field of environmental remediation. The interest and advantage of ferrite oxide could be attributed to its excellent properties such as narrow bandgap, nontoxicity, abundance of constituent element, low cost, and excellent electrical and catalytic properties (Liu et al., 2016). Ferrite-based perovskites attract attention due to their exceptional magnetic and electronic properties. They have intrinsic electric dipole moment due to a distortion in their crystal structures, which promotes separation of photogenerated charges during the photoexcitation process (Chen et al., 2017; AlSalka et al., 2019).

Most of the iron-based perovskites exhibit bandgaps within the visible region of the solar spectrum. For instance, bismuth iron oxide BiFeO₃ (BFO), a multi-ferroic member of the iron-based perovskites, is a typical case where simultaneously and spontaneously antiferromagnetic (TN = 643 K) and ferroelectric (TC≈1123 K) order coexist well above room temperature (Sosnowska et al., 1992; Sati et al., 2015). BiFeO₃ (BFO) with a rhombohedral distorted perovskite is a promising visible light responsive photocatalyst for organic pollutants degradation due to the suitable narrow bandgap (2.2–2.8 eV), excellent chemical stability, as well as intrinsic electric polarization (Ramadan et al., 2013). Charge-transfer (CT) transitions and spectroscopic measurements of the dielectric function of BiFeO₃ single crystal (Pisarev et al., 2009) showed a defect-free intrinsic bandgap of ~3.0 eV superimposed on a weak absorption band at 2.5 eV. This result signified the effect of defects and oxygen vacancies on the bandgap, and the shifting of the optical properties into the visible region. Electronic structure investigations have established the strongly hybridized nature of the valence band (Neaton et al., 2005; Clark and Robertson, 2007). However, some researchers reported that the photocatalytic activity of BFO was not impressive (Wang S. et al., 2016; Dixit et al., 2020), and they reported some drawbacks from BFO such as poor carrier mobility and rapid recombination of photogenerated electron–hole pairs. Based on these challenges, several strategies have been in place to improve its photocatalytic activity such as metal ion doping (Wang L. et al., 2016), heterostructure construction (Wang et al., 2017), structural control (Meng et al., 2016), and cocatalyst loadings (Behzadifard et al., 2018).

It has been recognized that metal ion doping assists in producing electron–hole trapping site which would probably accelerate the separation and transfer of the excited electron–hole pairs during the photocatalytic reaction (Wang S. et al., 2016; Dixit et al., 2020). Doping can also introduce surface defects such as oxygen vacancies by charge compensation arising between the dopant and the parent cation (Wang L. et al., 2016; Wang S. et al., 2016). Wang et al. (2017) studied the effects of oxygen vacancies induced by zirconium doping in bismuth ferrite for catalysis. The morphology features investigated by SEM and TEM showed the Zr-doped BFO with a smaller particle size of 50–150 nm significantly reduced aggregation as compared to the pristine BFO. The incorporation of Zr into BFO was confirmed by XPS. They reported that the optical absorption of the Zr-doped samples slightly shifted toward the shorter wavelength as opposed to the pristine BFO which has a strong absorption both in UV and visible light regions. A better photocatalytic performance in degradation of methyl orange (MO) using 2% Zr–BFO sample compared to the pure BFO and other Zr percentage loading samples was reported (Wang et al., 2017). Meng et al. (2016) studied the effect of the influence of lanthanum doping on photocatalytic properties of BiFeO₃ for phenol degradation. The catalyst was prepared by a one-step facile sol–gel method using citric acid as the chelating agent. The gel was calcined at 500°C for 2 h and then at 600°C for 1 h in a muffle furnace. From the XRD result, the BiFeO₃ structured was formed with the rhombohedral phase along with Biₓ₂FeO₄₀₀₉ impurity. As the wt% loading of La doping increases, the characteristic peak of the impurity disappeared. The result inferred that appropriate amount of La³⁺ doping can suppress the generation of impurity. SEM result also showed that 15 wt% La-doped BiFeO₃ assisted to decrease the catalyst particle size. The bandgap of the samples was studied using the Kubelka-Munk (K-M) formula. The authors suggested that La doping narrowed the bandgap.

Several studies have been done on ferrite-based perovskites, and majorities of them are in combination with other metals, nanomaterials, and other semiconductors with a purpose of extending light absorption range, retarding the electron hole recombination, and boosting the electron mobility toward efficient charge separation to achieve an excellent photocatalytic degradation of pollutants in water (Behzadifard et al., 2018; Malathi et al., 2018; Yahya et al., 2019; Bahmani et al., 2020; Dixit et al., 2020; Diyan et al., 2020; Haruna et al., 2020; Kumar P. et al., 2020).

**Titanate-Based Perovskites in Photocatalysis**

Titanate-based perovskite (MTiO₃) as a material has been explored in several applications. According to Alammar et al. (2015), they are promising materials for photocatalytic processes because of their excellent resistance to photocorrosion and high thermal stability. Ternary titanate-based perovskites such as CaTiO₃, BaTiO₃, and SrTiO₃ are wide bandgap titanate perovskite semiconductors with interesting electronic, optical, and magnetic properties (Alammar et al., 2015).
The preparation of titanate-based perovskite via the solid-state method often contains agglomerated particles of different sizes, morphologies, and impurities. Therefore, other methods where size, shape, and purity can be improved are favored. Titanate-based perovskites have offered applications in the area of photocatalytic hydrogen production and hydrocarbon reforming (Hbaeb et al., 2017). According to Zhang et al. (2007), the perovskite structure consisting of oxygen octahedral, such as TiO6, seems to play an important role for active photocatalysts, and the band edge positions, width of the conduction band, bandgap, and migration of photogenerated charge carriers as well as the photocatalytic activities are closely related to the distortion and the connectivity of the MO6 (M = Ti4+, Nb5+, and Ta5+) octahedra in perovskite titanates, niobates, and tantalates.

Titanate-based perovskites are reported to be photoactive materials, but their performance is impeded sometimes because of their wide bandgaps. However, titanate-based perovskites (such as SrTiO3 perovskite) exhibit good photostability and are thus applied in H2 production, solar cells, etc. Alammar et al. (2015) investigated the application of MTiO3 (M = Ca, Sr, and Ba) on the degradation of methylene blue using UV light. They reported that nitrogen-doped SrTiO3 showed good photocatalytic properties under visible light irradiation due to the formation of new states in the bandgap, allowing absorption of visible light. Hu et al. (2014) studied the photocatalytic activity of SrTiO3 (STO) synthesized by the autoclave hydrothermal method under the alkaline concentration and time. In photodegradation of the model pollutant-crystral violet (CV) dye, STO prepared with 3 M NaOH for 72 h at 130°C showed best photocatalytic performance with UV light. In tailoring the optical and photocatalytic properties of SrTiO3, Lu et al. (2017) successfully incorporated bismuth ferrite into it, forming a structure Sr1-xBixTi1-xFexO3. The synergetic effect resulted in more substantial visible light absorption, narrow bandgap, and enhanced photocatalytic performance. This study shows the possibility of tuning the bandgap of titanate-based perovskites into the visible light region. Lakhara et al. (2018) synthesized a visible light–responsive titanate-based perovskite by preparing a composite of TiO2 and NiTiO3 for photocatalytic degradation and hydrogen production activity. The photocatalytic activity of the nanocomposite was investigated by the photodegradation of rhodamine B dyes and tetracycline. With different calcination temperatures, the samples behaved differently. The optimized sample NT@750C nanocomposite displayed the highest degradation activity for RhB with about 75% total degradation within 2 h and nearly 58% degradation of tetracycline in 2 h with visible light. The total organic carbon (TOC) removal for both pollutants was lower than the respective decolorization rate, which is an indication of intermediate formation. The reusability test results for RhB dye showed that the photocatalyst can be reused for up to three cycles consecutively without major loss in the photocatalytic activity. In another study, Kiani et al. (2019) reported that a facile method was used to prepare magnesium titanate with magnesium ferrite nanocomposite as a support to improve the photocatalytic activity in degrading azo dyes. As a result of the heterostructure formed, the holes migrated to the valence band of MgFe2O4, while the electrons in the conduction band (CB) of MgFe2O4 migrated to the CB of MgTiO3, enabling an efficient charge separation and low recombination rate, hence allowing room for more charges to participate in redox reaction. Therefore, the photodegradation efficiency of the nanocomposite MgTiO3–MgFe2O4 increased about 30% relative to MgTiO3.

Combination power of microstructure and heterojunction techniques in a quest to remodel the inherent wide bandgap and enhance its visible light absorption capacity and photocatalytic performance cannot be down played. A multi-shelled cube structure of the CaTiO3–Bi2O3–Cl2 heterostructure was synthesized by Jiang et al. (2020) for degradation of tetracycline in water. They observed a greater percentage of tetracycline degradation within a short period with the multi-shelled hollow cube CaTiO3–Bi2O3–Cl2 heterostructure. They attributed the achievement to the larger surface area exhibited by the composite which led to more active sites than those participated in the redox reaction. There was a reduction of bandgap from 3.51 to 2.61 eV, thereby enhancing the absorption and utilization of visible light irradiation. The photochemical properties of the prepared samples which include photocurrent response, electrochemical impedance spectroscopy (EIS), photoluminescence spectra (PL), and linear sweep voltammery (LSV) showed that the heterostructured photocatalyst exhibited an excellent photostability, preferable electron–hole pair separation and longer lifetime, less charge migration resistance, and highest electric current densities.

Several researchers have reported titanate-based perovskite with heterostructure and co-doping. A majority of them have demonstrated an excellent photocatalytic performance as compared to their bare samples, and this is due to reduced bandgaps and efficient migration of charge pairs, hence reduced recombination rate which produces great catalytic activity within the redox reaction (Rosy and Kalpana, 2018; Jiang et al., 2019; Abdi et al., 2020; Chen X. et al., 2020; Dong et al., 2020; Han et al., 2020; Muˇzi´na et al., 2020; Tomar et al., 2020; Xiao et al., 2020; Yao et al., 2020; Yu et al., 2020). For instance, Abdi recorded 96% photodegradation of methyl orange within 150 min with Fe–La–doped SrTiO3 nanoparticle as compared to 5% from bare SrTiO3 (Abdi et al., 2020). In addition, these heterostructures contribute in generating more holes and superoxide O2·-, which are crucial oxidizing species involved in the catalytic system.

Tantalum and Other Perovskite-Based Materials in Photocatalysis

Tantalum-based perovskites (MTaO3) have received attention as a new class of material. They have been explored greatly in the area of water splitting. Kudo and Kato have carried out several studies on tantalum-related materials (Kato and Kudo, 1998; Kato and Kudo, 2001; Kudo et al., 2000). Tantalum-based perovskites (MTaO3) have also found applications in photocatalysis. Li and Zang (2011) prepared La-doped NaTaO3 via the hydrothermal method for the degradation of salfranine T dye under UV irradiation. The NaTaO3: La
N-doped NaTaO$_3$ was enhanced more than that of undoped because the presence of SrZrO$_3$ inhibited the oxidation of Sb$_2$O$_3$. The open circuit potential (OCP) was used to evaluate the stability of the samples. The heterostructure exhibited good photostability within 14 h irradiation of sunlight at pH 4 and COD removal percentage of 95.21% under the same conditions. The photocatalytic decolorization efficiency of N-doped NaTaO$_3$ was enhanced more than that of undoped because the interstitial nitrogen moved to the local state below the conduction band, and therefore excitation to the CB from the local state was convenient as a result of the “add on shoulder” on the N-doped NaTaO$_3$. They recorded complete decolorization within 14 h irradiation of sunlight at pH 4 and COD removal percentage of 95.21% under the same conditions.

N-doped potassium tantalate perovskite has also been used for the photocatalytic degradation of dye (Rao et al., 2018). The authors recorded reduction of bandgap and also extension of absorption of light from the UV region to the visible region which accelerates the photocatalytic activity. Modak and Ghosh (2014) successfully synthesized N (p-type) and F (n-type) doping in NaTaO$_3$ under visible light. Co-doping with N and F resulted in the formation of charge compensation and the iso electronic system on NaTaO$_3$. There was a reduction in bandgaps and visible light active material as a result of doping with N and F, which improved the photocatalytic activity. Apart from doping, the formation of heterojunction has also been reported for visible light photocatalytic applications. WO$_3$-wrapped NaTaO$_3$ prepared through a facile hydrothermal method was used to degrade tetracycline (Qu et al., 2015). An optimum percentage of 60.88% was recorded by the sample NaTaO$_3$/WO$_3$ which the authors attributed to an effective separation of the photogenerated electron–hole as well as the expansion of the absorption edge to the visible region due to the heterojunction structure. Some other types of perovskites that have found applications on photocatalysis are discussed below. Huerta-Flores et al. (2018) synthesized the SrZrO$_3$–Sb$_2$O$_3$ heterostructure for photocatalytic degradation of pharmaceutical compound. The heterostructure was successfully constructed using the impregnation method and was confirmed by XRD and SEM analyses. Results showed that they exhibited a weaker photoluminescence PL activity than Sb$_2$O$_3$ and SrZrO$_3$, which is an indication that there was adequate charge separation and mobility in the interface of SrZrO$_3$–Sb$_2$O$_3$, hence a minimized recombination rate. The open circuit potential (OCP) was used to evaluate the stability of the samples. The heterostructure exhibited good photostability because the presence of SrZrO$_3$ inhibited the oxidation of Sb$_2$O$_3$. The higher amount of electron accumulated in the conduction band in the heterostructure was evident because the change in the OCP negative value from dark to light was higher. It was also recorded that Sb$_2$O$_3$ induced a rapid electron transfer to the solution, which was effective in avoiding the charge carrier recombination, thereby increasing the use of electron–hole pairs in the redox reaction. Results from the Nyquist plot showed a smaller arc radius for Sb$_2$O$_3$ and SrZrO$_3$–Sb$_2$O$_3$ than the large semi-circle from SrZrO$_3$ material. The decrease in the arc radius indicates a faster interfacial charge transfer. The authors summarized that as a result of diminished electron–hole recombination in the SrZrO$_3$–Sb$_2$O$_3$ heterostructure, there was an increased availability of electron–hole separation which led to enhanced photodegradation of tetracycline.

Alkaline earth perovskite stannates such as ZnSnO$_3$, CaSnO$_3$, SrSnO$_3$, and BaSnO$_3$ have been widely used as photocatalysts. These materials have been found to be interesting for a number of potential applications in industry, such as components of dielectric ceramics; multifunctional signal sensors to detect temperature, humidity, and gas; as negative electrode active materials for long-life energy storage applications, and in the fabrication of ceramic boundary-layer capacitors (Zhang et al., 2006; Zhang et al., 2007; Fang et al., 2009). SrSnO$_3$ has been explored and also proven to be an effective photocatalyst owing to its powerful oxidation and reduction capabilities. However, it is associated with large bandgap and a high recombination rate of photogenerated electron–hole pairs. Therefore, the applications of its heterostructured composites have attracted attention in recent years. For instance, Venkatesh et al. (2020a) synthesized a heterostructure rGO–SrSnO$_3$ nanocomposite via hydrothermal methods. The authors recorded 97% methylene blue degradation and 80.66% for pure SrSnO$_3$. The optical property showed that a wide absorption band was identified at 220–270 nm for pure and rGO–SrSnO$_3$ composite, respectively. They recorded a reduced bandgap after incorporating rGO from 4.2 to 3.75 eV. Reduced graphene oxide has been an excellent electron acceptor with quick electron transport kinetics, and by that, the support of SrSnO$_3$ with rGO assisted in transferring the photo-induced electron to participate in the reaction, thereby leading to enhanced photocatalytic performance. Zhang et al. (2020) synthesized [K NbO$_4$]$_{0.9}$–[BaNi$_{0.5}$Nb$_{0.5}$O$_3$]$_{0.1}$ perovskite via a solid phase reaction method for methylene blue degradation. KBNNO perovskite has a bandgap of 1.39 eV, which is much smaller than that of the parent perovskite KNO. Incorporation of Ni$^{2+}$ and K$^+$ encourages oxygen vacancies and charge compensation, respectively. The photocatalytic degradation efficiency of KBNNO was 55% in 120 min. They concluded that the catalyst loading and dye concentration played a crucial role in the photocatalytic efficiency. Due to the octahedral tilting in the crystalline network of SnO$_6$, this distortion plays an important role in the migration of photogenerated charge carriers in SrSnO$_3$, CaSnO$_3$, and BaSnO$_3$ for photocatalytic degradation of pollutants (Honorio et al., 2020). Honorio et al. (2020) synthesized SrSnO$_3$ with ZrO$_2$ as a supporting semiconductor for photocatalytic degradation of a textile azo dye pollutant. Honorio discovered from SEM analysis that SrSnO$_3$ was uniformly dispersed on ZrO$_2$ which infers higher activity as a result of SrSnO$_3$ active phase even in a smaller amount. Therefore, they recorded 63 and 98% degradation at time 2 and 10 h, respectively. But, the doping
of SrSnO₃ with ZrO₂ did not significantly affect their bandgaps. They attributed this to be the presence of Sn(II) having lower binding energy may have occupied the inter-band states below the conduction band of Sn(IV). Some studies have been carried out on Tin-based perovskites for photocatalysis which have yielded excellent catalytic performance (Wang et al., 2009; Junploy et al., 2013; Wang et al., 2014).

### Photoelectrocatalysis

Photocatalysis has been widely utilized, and it is an important route for the degradation of organic waste. Its efficiency strongly relies on the catalyst. This technique has prominent advantages, including low cost and no secondary pollution. However, it has some drawbacks such as electron–hole pair recombination and catalyst recovery. Electrochemical oxidation localizes the semiconductor in the form of an electrode or substrate. Thus, the degradation of the organic pollutants occurs at the electrode surface or close to the electrode surface (hydroxyl radical in the bulk solution). This approach solves the catalyst recovery problem in photocatalysis. This electrochemical approach, however, requires high voltage and is prone to oxygen evolution, and the process is limited by mass transfer (Malpass et al., 2010; Siré et al., 2014; Brillas and Martinez-Huitle, 2015; Kusmierek and Chrzescijanska, 2015; Umukoro et al., 2017; Wang et al., 2018). The quest for improved techniques led to the emergence of photoelectrochemical oxidation or photoelectrocatalytic (PEC) processes. PEC is an electrolytic system containing a semiconductor-based anode that is simultaneously subjected to light illumination and a constant bias potential to the anode (Eanod), a constant cell voltage (Ecell), or a constant anodic current density (janod).

### Perovskite in Photoelectrocatalysis for Water Treatment

Perovskites have been extensively used in photocatalysis. In the area of photoelectrocatalysis (PEC), however, most applications of perovskites are in the energy sectors such as water splitting (Ni et al., 2007; Bin Adnan et al., 2018; Phoon et al., 2018) and solar cells (Muñoz-Gil et al., 2018; Fan et al., 2020). The application of perovskite in PEC for water treatment is still at its infancy. This review seeks to capture the recent application of perovskites in PEC and thus provide a valuable resource for materials, perovskites, and environmental research communities. Reports on PEC for water treatment are shown in Table 2 and reviewed in the following paragraphs. The chemistry of catalyst (perovskites) improvement strategies is similar to that of those explained earlier. Owing to the need to fabricate an anode (usually by depositing the semiconductor), different synthesis and electrode preparation methods peculiar to PEC are expected.

The first task in the application of perovskites in photoelectrocatalytic removal of organic pollutants in water is to understand the electrochemical and photoelectrochemical behaviors of the perovskites. To get such information, the perovskites have to be fabricated into an electrode. One of the common substrates for the deposition of perovskites for PEC application is the fluorine-doped tin oxide glass (FTO). For example, Fermin and coworkers studied the photoelectrochemical properties of LaFeO₃ nanoparticles by pasting an adhesive film of LaFeO₃ (along with other diluents) on a FTO coated glass (Celorrio et al., 2014). Although this work was not on water treatment, valuable data such as photocurrent responses obtained from this work are necessary characterizations that inform the potential applicability of the perovskites for PEC water treatments. With the use of a similar electrode preparation strategy, Zhang carried out a robust study on the photoelectrochemical behavior of heterostructured perovskite of the LaFeO₃–SrTiO₃ composite on FTO glass for NO removal (Zhang et al., 2017). The electrode was characterized along with the control electrodes of pristine LaFeO₃ (LFO) and

### Table 2

| Perovskite | Cocatalyst | Light source | Method | Pollutant | Substrate | Pollutant conc | Catalyst conc | Time, min | % Removal | Ref |
|------------|------------|--------------|--------|-----------|-----------|---------------|--------------|-----------|-----------|-----|
| BiFeO₃ | Sm, Pd | 300 W, Xe lamp | Conventional sol-gel | Methyl orange, phenol | FTO | 5 mg/L | 0.3 g | 120 | 8750.1 | Wang L. et al. (2016) |
| SrTiO₃ | TiO₂ | 300 W, Xe lamp | Hydrothermal/ anodization | Methylene blue | Ti | N/A | N/A | 20 | 99.93 | Huang J.-R. et al. (2014) |
| BiFeO₃ | TiO₂-NT | 500 W, Xe lamp | Citric sol-gel/ultrasonic immersion | Rhodamine | Ti | 20 mg/L | N/A | 150 | 100 | Zhu A. et al. (2014) |
| LaFeO₃ | SrTiO₂ | 420 nm LED | Ultrasonic spray pyrolysis | NO | FTO | 400 ppb | 0.1 g | N/A | 40 | Zhang et al. (2017) |

*Note: FTO stands for fluorine-doped tin oxide glass.*

The photoelectrocatalysis of heterostructured perovskite was carried out in aqueous solution containing Rhodamine B and NO. The anodic potential of the electrode was monitored under light illumination.
SrTiO$_3$ (STO). While all the photoanodes showed good photoelectric responses, the composite (LFO–STO) showed very pronounced response, indicating that heterojunction greatly promotes the separation of photo-induced electron–hole pairs and leads to the improved catalytic reaction rate. The authors concluded that the improved catalytic activity is due to the broad visible light harvest, enlarged surface area, and a suppressed surface charge recombination that emanated from the perfectly matched LaFeO$_3$ and SrTiO$_3$ interface and facile charge transfer.

Wang S. et al. (2016) also carried out photoelectrochemical studies to investigate the effect of a Pd cocatalyst and samarium doping in bismuth ferrite (BFO). Accordingly, the authors recorded a higher photocurrent response in Pd/BSFO (BSFO = Sm-doped BFO) samples than in BFO, Pd/BFO, and BSFO. They concluded that photocatalytic analysis and electrochemical analysis such as photocurrent response as shown in Figure 4 demonstrated that the combination of Pd loading and Sm doping could significantly promote the separation of photogenerated electron–hole pairs in the Pd/BSFO sample, thereby improving the photocatalytic activities.

As demonstrated by Arotiba and coworkers, such a photocurrent response from a photoanode can give a measure of how effective the electrode will be when used for PEC degradation (Umukoro et al., 2018; Orimolade et al., 2019; Orimolade et al., 2020; Orimolade and Arotiba, 2020).

One of the earliest work where a perovskite based photoanode was prepared and used for the PEC degradation of an organic pollutant is the work of (Zhu A. et al., 2014). The authors prepared TiO$_2$ nanotubes (TiO$_2$-NT) by anodic oxidation of titanium sheet and then deposited the BiFeO$_3$ nanoparticles from its precursor on the TiO$_2$-NTs via an ultrasonic-immersion strategy to form the BiFeO$_3$/TiO$_2$-NTs photoanode. The electrodes were extensively characterized by UV–vis diffuse-reflectance spectra, surface photovoltage, photoluminescence, electrochemical impedance spectroscopy etc. As shown in Figure 5 with the applied bias potential of 0.6 V, the photoanode displayed a pronounced efficiency as compared to photocatalysis and electrochemical analysis. This is in agreement with the electrochemical impedance that the photoanode BiFeO$_3$/TiO$_2$-NTs possessed a faster charge transfer across the electrode surface to the Ti substrate. These results point to a marked improvement in the photo-electrochemical properties of the BiFeO$_3$/TiO$_2$-NTs over TiO$_2$-NTs. These improvements were attributed to ease of charge transfer between the two materials, the ferroelectric properties of BiFeO$_3$ and the enhancement of charge separation. The BiFeO$_3$/TiO$_2$-NTs was used in the degradation of rhodamine B dye. A degradation of nearly 100% was achieved at the BiFeO$_3$/TiO$_2$-NTs photoanode after 150 min. This was significantly higher than when other techniques such as electrochemical oxidation, direct photolysis and photocatalysis process were employed. The schemes suggested by the authors for the electrode, bandgap alignment and schematic pathways are presented in Figure 6. From the diagram, the formation of heterostructure assisted in the formation of appropriate Fermi level, the application of bias potential channelled the electrons generated from the conduction band of BiFeO$_3$ to the conduction band of TiO$_2$-NTs. The separated, photogenerated electrons reacted with the surface chemisorbed O$_2$ to generate the strong oxidative species O$_2^-$, which combines with H$^+$ from solution to form H$_2$O$_2$. Finally, accumulated electrons in the counter electrode can react with H$_2$O to generate OH. This effective charge separation attributes to an excellent oxidation and reduction of the pollutants.

The positive coupling effect of combining TiO$_2$ and other semiconductors is considered as an efficacious approach to promote TiO$_2$ reactive properties. This enables the photogenerated charge carriers to migrate to the heterostructured interface to retard recombination.
Huang J.-R. et al. (2014) constructed a heterostructured nanotube with TiO$_2$/SrTiO$_3$ for PEC degradation of methylene blue (MB) dye. The photocurrent response among all the prepared catalysts TSr3 (TNT in Sr(OH)$_2$; 30 min hydrothermal time) showed the highest peak current, and it is twice as large as TNT2 (TiO$_2$ nanotube on Ti substrate). Their photocurrent response is such that when light is turned off, they returned instantly to zero; hence, the author concluded that the heterostructure composites under UV light can significantly promote the photogenerated electron/hole separation. The PEC degradation peak value was in good agreement with the rate constant $K$ with the optimal sample TSr3. The MB percentage degradation and rate constant were 99.93% and $0.38492 \times 10^{-4}$ min$^{-1}$, respectively. The authors attributed the result to be as a result of the positive cooperation of the high-reactive TiO$_2$ [001] facet with TiO$_2$/SrTiO$_3$ heterostructured interface which strongly inhibited the photogenerated electron/hole recombination.

**Effect of pH, Initial Concentration, and Catalyst Loadings of Perovskites in Photocatalysis and Photoelectrocatalysis**

**Effect of pH**

The pH of a solution influences the surface charge and protonation of the functional groups in a catalyst. It also promotes the efficiency and the performance of the process. Haruna et al. (2020) studied the pH of the solution for the degradation of 10 mg/L methylene blue using Bi$_{0.85-x}$M$_x$Ba$_{0.15}$FeO$_3$ (M = Na, K and x = 0, 0.1) at pH 3, pH 7, and pH 11. The observed improved photodegradation at pH 7 and pH...
11 of doped and undoped catalyst was attributed to the interaction of the highly negative oxide species and the anion which influenced the surface charge of the photocatalyst. Another study shows the degradation of tetracycline at pH 3, pH 5.60, and pH 10 using tungsten-doped BaTiO$_3$. The authors recorded the degradation rate of 90 and 80% for pH 10 and pH 5.60, respectively, after 3 h irradiation and 43% at pH 3. They concluded that increasing OH ions on catalyst surface promoted more OH$^-$ radicals which participated in the redox reactions (Demircivi and Simsek, 2019). Depending on the nature of the pollutant and the photocatalyst, the degradation efficiency varies with pH of the solution, hence the need to detect the optimum conditions that are favorable at any given time. Simsek et al. (2020) studied the effect of pH in photocatalysis and photocatalysis. They observed that the photocatalyst performed optimally at natural pH 6.5 compared with pH 3 and pH 10. According to Yao, the effect of pH and degradation of pollutant varies, and it is controversial (Haruna et al., 2020; Yao et al., 2004).

**Effect of Initial Concentration of Pollutants**

The increase in pollutant concentration could decrease the penetration of light into the solution for photocatalytic activity, thereby causing turbidity and opaqueness. Yahya et al. (2018) investigated the effect of initial concentration of humic acid using LaFeO$_3$. They observed the photocatalytic removal in the order of 98, 90, 85, and 86% for 10, 20, 30, and 40 g/L, respectively. It shows that at lowest initial concentration of humic acid, the photocatalytic activity was at its best. Therefore, they concluded that at a high pollutant dosage, the penetration of light needed to travel to the active site to activate the photodegradation was blocked, resulting in few active sites and poor photocatalytic activity. Also, a similar result was obtained by Pelin, where the degradation of tetracycline solution with an initial concentration of 5, 20, and 40 mg/L showed a degradation rate of 93, 80, and 47%, respectively (Demircivi and Simsek, 2019). Increase in turbidity, which can be due to high initial pollutant concentration is expected to reduce the efficiency of photoelectrocatalytic degradation of pollutants with perovskite-based photoanodes. This is because of insufficient light reaching the photoanode owing to poor penetration or scattering just as it is observed in photocatalysis. The issue of turbidity is not restricted to the pollutant concentration alone. Thus, for practicality, the process of simple filtration or sedimentation to remove suspended solids may precede PEC to improve the delivery of light onto the electrode or the catalyst.

**Effect of Catalyst Loadings**

Usually, at lower catalyst dosage, there are few active sites available for photodegradation, and at higher catalyst loadings, there are agglomeration, high turbidity, and scattering effects which lower the degradation efficiency in photocatalysis (Yahya et al., 2018; Yahya et al., 2020). Behzadifard et al. (2018) investigated the effect of CuO (10 wt%) SmFeO$_3$ composites for degradation of 10 mg/L rhodamine dye. They reported that the degradation rate of rhodamine increased with increasing catalyst loading from 0.05 to 0.15 g; however, at 0.20 g, the performance dropped, which they attributed to agglomeration and decrease in light penetration. It is therefore crucial to obtain the optimum value of catalyst loadings for cost-effectiveness and better photocatalytic performance.

**BANDGAP POSITIONS AND CHARGE TRANSFER MECHANISM OF PEROVSKITE OXIDES IN PHOTOCATALYSIS AND PHOTOELECTROCATALYSIS**

Bandgap calculation, tuning, and alignment are important in the characterization and in the prediction of the photocatalytic and photoelectrocatalytic efficiency of perovskite oxides (and other semiconductors) in water treatment. There are several ways of calculating band edge positions such as electronegativity-based calculation, density functional theory (DFT), the Mott–Schottky plot, dependence of photovoltage on pH, and photocurrent-potential measurement (Zhang and Jaroniec, 2018). Some band edge potentials of selected perovskite oxides discussed in this review are shown in Figure 7. Mukherjee et al. (2018) highlighted the effect of bandgap on photocatalytic improvement by the preparation of a composite of BFO and reduced graphene oxide (RGO). The conduction band (CB) and valence band (VB) edge potentials suggest band bending which arises in the equilibration of the Fermi level with the increase in the space region of the composite. The increase in the space region of the BFO–RGO composite resulted in the negative shift in the band edge potential, which facilitated the charge carrier concentration and consequently increased the chances of faster electron transfer, suppressed recombination, and better photoelectrocatalytic degradation (see Figure 8). In another report, Wang S. et al. (2016) explored the effect of rare earth (Sm) doping and noble (Pd) cocatalyst doping in BiFeO$_3$. The flat band potential measurement was calculated using the Mott–Schottky plot. Doping of bismuth ferrite with foreign atoms in their A, B, or O sites of the ABO$_3$ lattice has been proven to be an effective route to improving its photocatalytic properties (Mukherjee et al., 2018). From the band diagram in Figure 9, as reported by Wang L. et al. (2016), the hole could react with H$_2$O on the surface to generate OH for oxidation reaction because the VB potential of 1.5 wt% Pd–BSFO composite (+2.35 eV) is positive enough when compared to −OH/ OH$^-$ (+2.27 V vs NHE) as opposed to the CB potential of 1.5 wt% Pd–BSFO (+0.27 eV) which is less negative than the potential E° (O$_2$/O$_2$) $^-$ (−0.046 V vs NHE). Doping with rare earth metal served as an electron trapping specie to separate the photogenerated electron–hole from recombination, thereby promoting efficient charge carrier separation and consequently encouraging excellent...
photocatalytic activity. Behzadifard et al. (2018) studied the photocatalytic degradation of rhodamine and phenol. The band edge potentials were calculated using electronegativity methods. From the calculations, the VB and CB potentials for CuO were 1.97 and 0.65 eV and those of SmFeO₃ were 2.06 and 0.05 eV, respectively. Owing to the low negative CB potential value of SmFeO₃, adsorbed oxygen cannot be converted to −O₂. On the other hand, the CB potential of CuO is more positive than SmFeO₃; hence, electrons can migrate to the CB of CuO. In other words, CuO is acting as electron acceptor and is able to trap the electrons. Also, the CB potential of CuO (0.65 eV) is positive enough and closer to the potential for O₂/H₂O₂ (+0.695 eV), and the electrons are able to react with adsorbed oxygen to produce H₂O₂ and
subsequently $\cdot \mathrm{OH}$. The holes generated were transferred from the VB of SmFeO$_3$ to CuO because the VB potential of SmFeO$_3$ (+2.06) was not high enough to oxidize the adsorbed $-\mathrm{OH}$ ($-\mathrm{OH}/\mathrm{OH} = +2.38$ eV) and $\mathrm{H}_2\mathrm{O}$ ($\mathrm{H}_2\mathrm{O}/\mathrm{OH} = +2.72$ eV) to $\mathrm{OH}$; hence, holes in SmFeO$_3$ could have directly oxidized the organics had it enough potentials. The formation of the heterojunction promoted the charge separation and suppressed the recombination of charge carriers.

The mechanism of reaction was summarized in Eqs. 1–4 (Behzadifard et al., 2018; Zhang and Jaroniec, 2018).

$$\mathrm{CuO}/\mathrm{SmFeO}_3 + \mathrm{hv} \ (\text{visible light}) \rightarrow e^- \ \mathrm{CB} \ (\mathrm{CuO \ and \ SmFeO}_3)$$
$$+ h + \mathrm{VB} \ (\mathrm{CuO \ and \ SmFeO}_3), \quad (1)$$

$$2e^- \ \mathrm{CB} (\mathrm{CuO}) + 2\mathrm{H}^+ + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O}_2, \quad (2)$$

$$\mathrm{H}_2\mathrm{O}_2 + e^- \rightarrow \cdot\mathrm{OH} + \mathrm{OH}, \quad (3)$$

Pollutant + $\mathrm{OH}/h^+ \rightarrow$ Intermediates $\rightarrow$ degradation products. \quad (4)

**CONCLUSION AND RECOMMENDATION**

In this review, we discussed the recent progress in the field of photocatalysis and photoelectrocatalysis based on perovskite and perovskite-related materials. Recently, research has geared toward photocatalytic materials that are capable of absorbing light in the visible region. Perovskite and perovskite-related...
Furthermore, in order to maximize the degradation efficiency of organic pollutant due to their fascinating properties. Few photoelectrocatalysis degradation reports discussed here show that synergy of photocatalysis and electrosynthesis promotes better degradation performance. Reports have also shown that immobilizing catalyst onto substrate and application of bias potential aid in catalyst recovery, reduce electron–hole recombination, and increase charge resistance. In particular, the formation of perovskites as photoanodes through novel nanostructure engineering, surface modification with exotic element doping or cocatalyst loading, and innovative system design based on heterojunction configuration are excellent strategies for improving light harvest, charge separation, as well as surface reaction kinetics as compared to the single perovskites, for example, BiFeO₃ doped with Sm and Pd (Wang S. et al., 2016). Agreeably, great progress has been made over the years; however, for ultimate realization of the inherent potential in perovskite, more work needs to be done in discovering new perovskites for photoelectrocatalysis. Furthermore, in order to maximize the degradation efficiencies in vast composition of organic pollutants, other advanced oxidation processes such as sono-photoelectrocatalysis and thin-film slurry flat-plate photoreactor. J. Solid State. Chem. 286, 121304. doi:10.1016/j.jssc.2020.121304

Author Contributions

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Therefore, for the advancement of perovskite-based material for photoelectrocatalysis treatment of water, continuous research into a better crystal structure for stability as well as performance improvement is essential. Perovskites with long-term stability and exceptional optical and electrochemical properties are essential for sustainability.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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