PH-MEDIATED COLLECTIVE AND SELECTIVE SOLAR PHOTOCATALYSIS BY A SERIES OF LAYERED AURIVILLIUS PEROVSKITES

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ABSTRACT: Semiconductor photocatalysis under natural sunlight is an emergent area in contemporary materials research, which has attracted considerable attention toward the development of catalysts for environmental remediation using solar energy. A series of five-layer Aurivillius-phase perovskites, Bi₅AT₁₄FeO₁₈ (A = Ca, Sr, and Pb), are synthesized for the first time. Rietveld refinements of the powder X-ray diffraction data indicated orthorhombic structure for the Aurivillius phases with Fe largely occupying the central octahedral layer, whereas the divalent cations (Ca, Sr, and Pb) are statistically distributed over the cubo-octahedral A-sites of the perovskite. The compounds with visible-light-absorbing ability (Eg ranging from ~2.0 to 2.2 eV) not only exhibit excellent collective photocatalytic degradation of rhodamine B–methylene blue (MB) and rhodamine B–rhodamine 6G mixture at pH 2 but also show almost 100% photocatalytic selective degradation of MB from the rhodamine B–MB mixture at pH 11 under natural solar irradiation. The selectivity in the alkaline medium is believed to originate from the combined effect of the photocatalytic degradation of MB by the Aurivillius-phase perovskites and the photolysis of MB. Although a substantial decrease in MB adsorption from the mixed dye solution (MB + RhB) together with slower MB photolysis at the neutral pH makes the selective MB degradation sluggish, the compounds showed excellent photocatalytic degradation activity and chemical oxygen demand removal efficacy toward individual RhB (at pH 2) and MB (at pH 11) under sunlight irradiation. The catalysts are exceptionally stable and retain good crystallinity even after five successive cyclic runs without any noticeable loss of activity in both the acidic and alkaline media. The present work provides an important insight into the development of layered perovskite photocatalysts for collective degradation of multiple pollutants and selective removal of one or multiple pollutants from a mixture. The later idea may open up new possibilities for recovery/purification of useful chemical substances from the contaminated medium through selective photocatalysis.

1. INTRODUCTION

Utilization of inexpensive and inexhaustible solar energy for the degradation of harmful pollutants (environmental remediation) and production of hydrogen (a source of renewable energy) by the water-splitting reaction through semiconductor photocatalysis have attracted immense research interest in recent times. Improper management of effluents from industries, such as textile, printing, plastic, cosmetics, coating, paper, and rubber, causes serious threat to the environment. Moreover, according to the World Health Organization (WHO) report, 25% of human health diseases arise because of the long-term exposure of environmental pollutants that are present in soil, air, and water. Therefore, neutralization, degradation, and/or mineralization of harmful pollutants released from the industries are vital for a cleaner environment and sustainable living.

Ideally, an efficient visible-light-driven photocatalyst that harvests solar energy will have wide-ranging applications not only in environmental remediation, inclusive of organic pollutant degradation, water disinfection, indoor air purification through volatile organic compound removal, and self-cleaning of surfaces, but also in the area of renewable energy generation in the form of hydrogen by water splitting. Since Fujishima and Honda’s revolutionary discovery of photoelectrochemical water decomposition on the TiO₂ electrode under UV irradiation in 1972, semiconductor photocatalysis has become one of the most widely investigated areas for the development of efficient photocatalysts. Subsequently, different cationic and anionic substitutions on TiO₂ and other oxides of d⁰ transition metals together with the main group elements have been extensively investigated for developing newer and better catalysts. In this context, exploration of perovskite-based oxides for photocatalytic energy conversion and environmental remediation is noteworthy. Often, the catalysts are active only under UV
light, whereas for harvesting abundant sunlight, visible-light activity is essential.

Recently, a lot of attention has been given to oxides with layered structures that are active in the visible light, especially to the Aurivillius family that contains Bi as one of the constituent elements.\(^\text{39-43}\) The presence of Bi is claimed to be advantageous in two respects. First, it enhances the likelihood of visible-light absorption by pushing up the valence band (VB) edge because of the hybridization of Bi 6s with O 2p orbital. Second, the highly dispersed nature of the Bi 6s−O 2p hybridized VB results in the high mobility of the photogenerated holes.\(^\text{25,26}\) The Aurivillius family of oxides are well-known variants of layered perovskites that form with a regular intergrowth of fluorite-like (Bi\(_2\)O\(_2\))\(^\text{24}\) layers with the perovskite (A\(_n-1\)B\(_n\)O\(_{3n+1}\))\(^{2-}\) blocks, where \(n\) represents the number of corner connected octahedral layers. For instance, Bi\(_2\)WO\(_6\) and Bi\(_2\)MoO\(_6\) are classic examples of \(n = 1\) member of the Aurivillius family, which were studied extensively as visible-light-driven photocatalysts.\(^\text{27-30}\) However, because of the lack of higher-order members (\(n = 2\) and \(4\)−\(5\)), similar photocatalytic studies are limited.\(^\text{31-33}\) However, the five-layer (\(n = 5\)) Aurivillius phase, Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\), was synthesized and investigated for its ferroelectric, magnetic, and optical properties.\(^\text{34,35}\) Additionally, the rare earth (La, Sm, Gd, and Dy)−substituted Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\) was explored for its magnetic and magnetolectric properties.\(^\text{36,37}\) Recently, the study on the five-layer Aurivillius phase, Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\), investigating the effect of La substitution on phase formation, structure, and its consequences on photocatalysis was reported by our group.\(^\text{33}\) Thus, higher-order Aurivillius-layered perovskites and their solar photocatalysis constitute an important area for the exploration of single semiconductor oxide photocatalysts without heterojunction formation or cocatalyst loading.\(^\text{23,31-33}\)

Although removal of harmful pollutants from wastewaters by photocatalysis is widely investigated, most of the studies have focused on the degradation of a single dye as a pollutant. As the wastewater released from various industries is contaminated with multiple dyes rather than a single dye, it is desirable to test the efficiency of a catalyst toward the collective removal of multiple dyes from a mixture. Therefore, the study of the collective photocatalytic removal of pollutants from a mixture is challenging, and such studies are rare in the current literature. This will be helpful in the development of photocatalysts active for the treatment of real wastewater disemboqned from various industries into water bodies. Likewise, selective degradation of one pollutant from a mixture may lead to the development of photocatalytic processes for the recovery/purification of useful chemical substances from a contaminated one. Only few reports of selective photocatalytic oxidation of organic compounds and contaminants with TiO\(_2\)-based oxides are known in the literature.\(^\text{38-44}\) The reported photocatalytic selectivity was achieved either by nanostructuring,\(^\text{40,42,43}\) constructing molecular recognition sites,\(^\text{41}\) or by functionalizing nanosheets.\(^\text{44}\) However, in all the above selective photocatalysis reported so far, mostly UV light has been utilized. Very recently, visible-light-driven selective dye degradation was reported over hierarchical mesocrystals of AgIn(WO\(_4\))\(_2\)\(^\text{45}\) nano CuWO\(_4\) and Cu\(_2\)MoO\(_6\).\(^\text{46}\) In another report, selective methylene blue (MB) degradation over CuFe\(_2\)O\(_4\) nanoparticles was mediated by NaBH\(_4\).\(^\text{47}\) In view of the foregoing and considering RhB, MB, and Rh6G as model dye systems, we thought it would be appealing to achieve collective and selective photocatalysis from the mixture of RhB−MB and RhB−Rh6G under sunlight irradiation using a single semiconductor photocatalyst.

Here, a series of five-layer Aurivillius phases, Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\)), are envisaged by both perovskite A- and B-site cosubstitution through the cationic charge manipulation of Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\). The synthesis, characterization, and pH-mediated collective and selective solar photocatalytic degradation of RhB−MB−Rh6G dye systems over the perovskite catalysts are reported. The reasons for selectivity and enhanced activity are elucidated based on dye adsorption, zeta-potential, octahedral distortion, and mechanistic investigations.

2. RESULTS AND DISCUSSION

2.1. Powder X-ray Diffraction (P-XRD) Analysis. The P-XRD patterns of Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\)) are shown in Figure 1. A preliminary analysis of the P-XRD data by comparison with standard JCPDS files reported in the literature indicated the formation of five-layer Aurivillius phases similar to Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\).\(^\text{30}\) Table 1 lists the unit cell parameters of Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\)) series along with the band gap energies to determine the electronic structure of the materials.

![Figure 1. P-XRD patterns of (a) Bi\(_5\)CaTi\(_4\)FeO\(_{18}\), (b) Bi\(_5\)SrTi\(_4\)FeO\(_{18}\), and (c) Bi\(_5\)PbTi\(_4\)FeO\(_{18}\).](image)

Table 1. Lattice Parameters and Band Gap Energies of Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\))

| compound      | lattice parameters (\(\text{Å}\)) | band gap (eV) |
|---------------|---------------------------------|---------------|
|               | \(a\) | \(b\) | \(c\) | \(E_g (1)\) | \(E_g (2)\) |
| Bi\(_5\)CaTi\(_4\)FeO\(_{18}\) | 5.451(1) | 5.438(1) | 49.10(1) | 2.09 | 2.61 |
| Bi\(_5\)SrTi\(_4\)FeO\(_{18}\) | 5.475(1) | 5.466(1) | 49.29(1) | 2.12 | 2.72 |
| Bi\(_5\)PbTi\(_4\)FeO\(_{18}\) | 5.472(1) | 5.462(1) | 49.69(1) | 2.11 | 2.66 |

Sr, and Pb) are determined by least-squares refinement of all the observed diffraction lines in the orthorhombic \(P2mm\) (no. 42) space group. A close look at the lattice parameters of Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\)) series shows an expansion in the \(c\)-parameter when \(A\) varies from Sr to Pb, whereas a slight contraction is observed for the Ca analogue as compared to the parent Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\).

The crystal structure of Bi\(_\alpha\)ATi\(_\beta\)Fe\(_\gamma\)O\(_{18}\) (\(A = \text{Ca, Sr, and Pb}\)) is determined by Rietveld refinements of the P-XRD data. The initial model for the structure refinement of Bi\(_5\)SrTi\(_4\)FeO\(_{18}\) was constructed using the atomic coordinates of Bi\(_5\)Ti\(_3\)Fe\(_2\)O\(_{18}\) (\(P2mm\) space group) wherein Fe\(_\gamma\) completely occupies the...
central octahedral layer and the remaining octahedral layers are occupied by Ti$^{4+}$; Sr$^{2+}$ is distributed statistically over all the Bi$^{3+}$ sites in the perovskite block keeping the [Bi$_2$O$_2$]$^{2+}$ layer exclusively occupied by Bi$^{3+}$. Several trial refinement runs with other models, where Fe$^{3+}$ was statistically distributed over all the perovskite B-sites and Sr$^{2+}$ over all the perovskite A-sites and [Bi$_2$O$_2$]$^{2+}$ layers, resulted in higher reliability factors. The observed, calculated, and difference profiles of the final Rietveld refinement fit are shown in Figure 2. The refined atomic positions, occupancies, and thermal parameters are given in Table 2. Figure 3 shows the structure of Bi$_5$SrTi$_4$FeO$_{18}$ drawn using the refined atomic positions.

![Figure 2. Rietveld refinement of the structure Bi$_5$SrTi$_4$FeO$_{18}$ from P-XRD data. Observed (+), calculated (−), and difference (bottom) profiles are shown. The vertical bars represent the Bragg positions.](image)

### Table 2. Atomic Position, Site Occupancy, and Thermal Parameters of Bi$_5$SrTi$_4$FeO$_{18}$

| atom      | x      | y      | z      | $B_{eq}$ | occ. |
|-----------|--------|--------|--------|----------|------|
| Bi(1)     | 0.5490(1) | 0      | 0.7247(1) | 1.32     | 2    |
| Bi(2)/Sr(2)| 0.5528(1) | 0      | 0.5425(1) | 1.32     | 1.5/0.5 |
| Bi(3)/Sr(3)| 0.5418(2) | 0      | 0.6301(2) | 1.32     | 1.5/0.5 |
| Ti(1)     | 0.5155(1) | 0      | 0.8341(1) | 0.83     | 2    |
| Ti(2)     | 0.5115(3) | 0      | 0.9171(1) | 0.83     | 2    |
| Fe        | 0.5    | 0      | 0      | 0.83     | 1    |
| O(1)      | 0.25   | 0.75   | 0      | 3.1      | 2    |
| O(2)      | 0.75   | 0.25   | 0.25   | 3.1      | 2    |
| O(3)      | 0.5    | 0.7998(3) | 3          | 3.1      | 2    |
| O(4)      | 0.5    | 0.8806(1) | 3          | 3.1      | 2    |
| O(5)      | 0.5    | 0.9635(1) | 3          | 3.1      | 2    |
| O(6)      | 0.5    | 0.25   | 0.4202(1) | 3.1      | 4    |
| O(7)      | 0.25   | 0.25   | 0.3444(1) | 3.1      | 4    |

*Space group P2$_1$2$_1$2$_1$, $a = 5.4681(4)$, $b = 5.4585(4)$, $c = 49.164(2)$ Å, $R_{Bragg} = 3.2\%$, $R_I = 1.8\%$, $R_F = 5.1\%$, $R_{wp} = 6.5\%$, and $\chi^2 = 1.8$.*

Similar structure refinements for Bi$_5$CaTi$_4$FeO$_{18}$ and Bi$_5$PbTi$_4$FeO$_{18}$ based on the same model structure also gave satisfactory fits (Figure S1 in the Supporting Information). However, because of several free oxygen positions, a simultaneous refinement of positional and thermal parameters for all the atoms that are in a general position could not be achieved. Thus, for a good profile match, the positional parameters were refined one by one in a stepwise manner, whereas the oxygen thermal parameters were restricted to the same value for all the oxygens, Bi/Sr and Ti/Fe. To achieve convergence in the case of Ca analogue, one of the Ti1 coordinates was kept fixed. However, for more accurate determination of oxygen positions of these Aurivillius phases, a neutron diffraction study would be necessary. The refined atomic positions, occupancies, and thermal factors for Ca and Pb compounds are given in Tables S1 and S2 in the Supporting Information.

### 2.2. Field Emission Scanning Electron Microscopy (FE-SEM), Energy-Dispersive X-ray Spectroscopy (EDS), and Elemental Mapping Analysis

FE-SEM and the corresponding EDS of Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb) are shown in Figure S2 in the Supporting Information. All the compounds show morphological homogeneity of the crystallites in the entire region of image exhibiting platelike microstructures though with a fairly large extent of particle aggregation. Moreover, there is a large variation in the size of crystallites ranging from several hundred nanometers to few micrometers. Elemental compositions obtained from EDS at several crystallites of the imaged area show excellent compositional uniformity and agree with the nominal elemental compositions. The elemental mapping (Figure 4) carried out in a selected rectangular area of Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb) showed homogeneous and uniform distribution of all the elements in the compounds.

### 2.3. Transmission Electron Microscopy (TEM) Analysis

The crystalline nature of Bi$_5$SrTi$_4$FeO$_{18}$ was confirmed by TEM and high-resolution TEM (HR-TEM) studies. The HR-TEM image (Figure 5a) clearly revealed the layered intergrowth nature of the Aurivillius phase consisting of alternating layers of the perovskite blocks interleaved by [Bi$_2$O$_2$]$^{2+}$ units. Moreover, the lattice fringes of 4.925 nm shown in the HR-TEM image (Figure 5b) agree with the c-parameter of Bi$_5$SrTi$_4$FeO$_{18}$. The indexing of few representative spots in the selected area electron diffraction (SAED) pattern (Figure 5c) is consistent with the crystal system and $d_{hkl}$s assigned by the P-XRD data analysis.

### 2.4. UV–Vis Diffuse Reflectance Spectra (DRS) Analysis

The optical absorption spectra (Figure 6a) of Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb) show visible-light
absorption by all the compounds with the absorption edges extending beyond 500 nm. There are indeed two characteristic absorptions similar to those observed for Bi$_5$La$_x$Ti$_3$FeO$_{15}$ ($x = 1, 2$) and Bi$_6$La$_x$Ti$_3$Fe$_2$O$_{18}$ ($x = 0, 1$). The band gap energies of the compounds are calculated from the Tauc plots (Figure 6b). The best fit for $(\alpha h\nu)^{1/2}$ versus $h\nu$ was obtained for $n = 2$, suggesting probably an indirect band gap transition, similar to those of Bi$_5$La$_x$Ti$_3$FeO$_{15}$ and Bi$_6$La$_x$Ti$_3$Fe$_2$O$_{18}$. The estimated band gap energies (Table 1) of the compounds in the range 2.0–2.2 eV are intriguing to explore their potential for sunlight-driven photocatalysis.

2.5. Photoluminescence (PL) Analysis. For comparing the efficacy of the photogenerated charge carrier separation or the $e^-+h^+$ recombination in Bi$_5$ATi$_4$FeO$_{18}$ ($A = \text{Ca, Sr, and Pb}$), PL spectra were recorded at an excitation wavelength of 350 nm. A comparatively lower PL intensity is indicative of relatively slower or inefficient recombination, thereby suggesting better charge carrier separation or longer lifetime for the electrons and holes, which in turn enhances the photocatalytic activity. As portrayed in Figure S3 in the Supporting Information, all the compounds show broad PL emission ranging from 400 to 600 nm with a peak of around 470 nm. However, the differences in PL intensities are very subtle, which is reflective of the electronic structure and composition of the compounds. The compositional difference in the compounds will not affect the frontier band levels as the electronic states from Ca and Sr are known to be deep inside the VB, thus not affecting the PL properties largely. According to the PL spectra, one might expect a higher activity for Bi$_5$SrTi$_4$FeO$_{18}$, but one need to consider several other factors to explain the overall activity of the catalysts (see the next section).

2.6. Photocatalytic Activity. The activity of the compounds, Bi$_5$ATi$_4$FeO$_{18}$ ($A = \text{Ca, Sr, and Pb}$), in solar photocatalysis was evaluated by dye removal/degradation from aqueous solutions taking RhB, MB, and a mixture of RhB–Rh6G as model systems. The amount of compounds used in the degradation was according to our dosage optimization study (see the Supporting Information and

Figure 4. (a) Bright field image and the corresponding EDS elemental mapping of (b) Bi, (c) Ca, (d) Ti, and (e) Fe in Bi$_5$CaTi$_4$FeO$_{18}$ and (f–j) and (k–o) represent bright field image and elemental mapping for Bi$_5$ATi$_4$FeO$_{18}$ ($A = \text{Sr and Pb}$) in the same order where the third vertical panel represents the A cations, Sr and Pb, respectively.

Figure 5. (a) TEM image, (b) HR-TEM image, and (c) SAED pattern of Bi$_5$SrTi$_4$FeO$_{18}$.

Figure 6. (a) UV–vis DRS of Bi$_5$ATi$_4$FeO$_{18}$ ($A = \text{Ca, Sr, and Pb}$). (b) Corresponding Tauc plots for the calculation of band gap.
Figure S4). UV−vis spectral measurements recorded with time during the degradation of a RhB−MB mixed dye solution show a decrease in the intensity of the characteristic absorption peaks for the MB leaving those of the RhB nearly unchanged at pH 7 and 11 (Figures 7a and S5), whereas in the case of the RhB−Rh6G mixture, the main absorption peak for RhB (Figure 7c) disappears at a faster rate than that of Rh6G at pH 2 under sunlight irradiation. This indicates a selective degradation of MB and RhB from the aqueous mixtures of RhB−MB and RhB−Rh6G, respectively. Interestingly, all the compounds show selective degradation but up to different extents as a function of time. Surprisingly, the photostability studies of the dyes at different pHs show that RhB is stable at all pH (2, 7, and 11), whereas MB appears to undergo self-degradation/photolysis at neutral (pH 7) and basic (pH 11) pH under sunlight (Figure S7 in the Supporting Information). Thus, the photodissociation of MB is considered as a side reaction that occurs parallel to the photocatalytic degradation of MB at pH 7 and 11.

To ascertain the true rate of photocatalysis for the selective degradation of MB from the mixture of RhB−MB, the corrected rate for MB degradation is calculated by subtracting the photolysis part from the total absorbance data of MB degradation (Figure 8). Figure 8a shows ln(C0/C) versus irradiation time plots for MB degradation from the RhB−MB mixture at pH 7 by Bi5SrTi4FeO18, and the degradation rate constants (k) are 0.0108, 0.0048, and 0.0030 min−1 for total degradation, photolysis, and photocatalysis, respectively. Similarly, the degradation rate constants (k) at pH 11 are 0.0409, 0.0072, and 0.0095 min−1, respectively (Figure 8b). As the rate of MB degradation from the RhB−MB mixture is faster at pH 11 than that at pH 7, the same is reflected in the rate constants. Noticeably, the rate of photocatalysis is faster than that of photolysis at pH 11, whereas the reverse is true at pH 7. Moreover, there is more than three times increase in the rate of photocatalysis at pH 11, making the MB degradation rapid and 100% selective over Bi5SrTi4FeO18.

Interestingly, selective degradation of RhB from the RhB−Rh6G aqueous mixture can be envisaged at pH 2 within 40 min of solar irradiation over Bi5SrTi4FeO18. However, complete and collective removal of RhB and Rh6G from the mixture is accomplished in 120 min (Figure 7b). Moreover, complete and collective degradation of the RhB−MB mixture is also achieved at pH 2 within 160 min of solar irradiation over Bi5SrTi4FeO18 (Figure 7b). However, in a similar
experiment, Bi₅PbTi₄FeO₁₈ showed complete degradation of MB and up to 69% degradation of RhB, whereas the corresponding Ca analogue exhibited only up to 65% of MB and 40% of RhB degradation after 180 min of solar irradiation (Figure S6 in the Supporting Information). In the later cases, the λ_max of RhB underwent a hypsochromic shift, indicating de-ethylation of RhB during the degradation.

Further, to explore the ability of the catalysts in individual MB and RhB degradation, a series of photocatalytic experiments with single dye solutions were conducted under sunlight irradiation at different pHs. The RhB degradation and subsequent % chemical oxygen demand (COD) removal (Figure 9) unveiled complete RhB degradation within 30−60 min of sunlight irradiation at pH 2. Moreover, the RhB decoloration kinetics (Figure 9a) is more or less concordant with the % COD removal, indicating excellent dye mineralization. The degradation rate constants (k) (Figure 9b) are 0.085, 0.150, and 0.138 min⁻¹ for Bi₅CaTi₄FeO₁₈, Bi₅SrTi₄FeO₁₈, and Bi₅PbTi₄FeO₁₈, respectively. Despite complete RhB degradation at pH 2, the catalysts did not show RhB degradation to any significant extent at pH 7 and pH 11, indicating negligible photocatalysis in neutral and alkaline media (Figure S9 in the Supporting Information). On the contrary, the individual MB degradation over Bi₅ATi₄FeO₁₈ (A = Ca, Sr, and Pb) has revealed fastest degradation at pH 11, moderate degradation at pH 2, and very slow degradation at pH 7 (Figure S10 in the Supporting Information). The complete degradation of MB over the catalysts is observed at pH 11 within 50−60 min of sunlight irradiation, and the % COD removal indicated excellent dye mineralization ability (Figure 10a). The rate constants (k) (Figure 10b) for the total MB degradation at pH 11 are 0.069, 0.113, and 0.077 min⁻¹ for Bi₅CaTi₄FeO₁₈, Bi₅SrTi₄FeO₁₈, and Bi₅PbTi₄FeO₁₈, respectively. Apparently, these rate constants do not represent the rate for pure photocatalytic mechanisms because the degradation also proceeds via photolysis of MB. Moreover, at pH 2, Bi₅SrTi₄FeO₁₈ and Bi₅PbTi₄FeO₁₈ showed complete MB degradation within 130−150 min, whereas Bi₅CaTi₄FeO₁₈ showed only ~55% MB degradation after 180 min of solar irradiation (Figure S10a in the Supporting Information). At pH 7, only 30, 45, and 37% of MB are degraded (Figure S10b in the Supporting Information) by Bi₅CaTi₄FeO₁₈, Bi₅SrTi₄FeO₁₈, and Bi₅PbTi₄FeO₁₈, respectively, in 180 min. The rate of photocatalytic degradation for individual MB and RhB over these layered Aurivillius perovskites follows the order: Bi₅CaTi₄FeO₁₈ < Bi₅PbTi₄FeO₁₈ < Bi₅SrTi₄FeO₁₈.

2.7. Detection of Reactive Species. To identify the dominant reactive species responsible for the photocatalytic degradation of MB and RhB over Bi₅SrTi₄FeO₁₈, a series of scavenger tests were performed. The photocatalytic RhB degradation efficiency of Bi₅SrTi₄FeO₁₈ in the presence of scavengers is shown in Figure 11. The rate of degradation at pH 2 is substantially reduced on addition of ammonium.
oxalate (AO, an h+ scavenger) to the dye–catalyst suspension as compared to that in the absence of any scavenger. However, a moderate extent of retardation in the RhB degradation is noticed with the addition of benzoquinone (BQ, an O2•− scavenger) to the dye–catalyst suspension and the addition of t-BuOH (•OH scavenger) caused the rate retardation only to a small extent at this pH. The above findings are consistent with the fact that h+ and O2•− are active contributors in the photocatalytic RhB degradation over Bi5SrTi4FeO18 in the acidic medium and •OH plays an assistant minor role in the degradation. Moreover, the same reactive species are active for the MB degradation at pH 11 (Figure S11 in the Supporting Information).

2.8. Catalyst Reusability and Stability. The reusability and stability of the catalysts are important parameters to be assessed for making the semiconductor photocatalysis attractive and cost-effective for dye wastewater treatment. The photocatalytic cycle test (Figure 12a) performed over Bi5SrTi4FeO18 (the best among all the catalysts studied here) for RhB degradation shows excellent recyclability up to four cycles and only a minor decrease (∼3%) in the activity during the fifth cycle attributable to the unavoidable loss of catalysts during recycling. The catalytic cycle study suggests very good cyclability without any noticeable loss in the activity of the photocatalysts.

The stability of the catalyst is assessed by P-XRD (Figure 12b) and X-ray photoelectron spectroscopy (XPS) analysis (Figure 13) of Bi5SrTi4FeO18 recovered after the cyclic runs. The P-XRD pattern indicated excellent retention of phase purity and crystallinity signifying no photodecomposition of the oxide while maintaining its structural integrity during photocatalysis (Figure 12b). Moreover, the cycle test for the individual MB degradation also pointed toward very good recyclability at pH 11 (Figure S12 in the Supporting Information). The postcatalytic P-XRD analysis of the Ca and Pb analogues also demonstrated good catalyst stability under the reaction conditions (Figure S13 in the Supporting Information). XPS data of Bi5SrTi4FeO18 recorded before and after the photocatalytic degradation of RhB–Rh6G (Figure 13) also ascertained excellent chemical stability of all the elements present in the oxide.

Figure 12. (a) Photocatalytic cycle study of Bi5SrTi4FeO18 for RhB degradation. (b) P-XRD patterns of Bi5SrTi4FeO18 recorded before and after five successive photocatalytic RhB degradations.

Figure 13. XPS spectra of (a) Bi 4f, (b) Sr 3d, (c) Ti 2p, (d) Fe 2p, and (e) O 1s of Bi5SrTi4FeO18 before and after the photocatalytic degradation of the RhB–Rh6G mixture at pH 2.

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the presence of Fe\(^{3+}\) in the compound both in its pristine form and after photocatalysis.

Similar spin–orbit-coupled doublet (3d_{5/2} and 3d_{3/2}) features are also evident for Sr 3d (Figure 13b) and Ti 2p spectra (Figure 13c). The binding energy of 457.6–457.8 eV for Ti 2p_{3/2} states and 463.4–463.6 eV for Ti 2p_{1/2} states corresponds to the presence of Ti\(^{4+}\) ions with an additional overlapping peak at 465.7 eV because of Bi 4d_{3/2}. \(^{51}\) Moreover, the deconvoluted spectra of O 1s (Figure 13e) corroborate well with two types of hybridized states of O with binding energies ranging between 529.3 and 529.4 eV corresponding to Bi and Ti, respectively.

2.9. Mechanism of Photocatalytic Activity. The adsorption is the first and foremost step in any heterogeneous catalytic process and the photocatalytic degradation of dyes is no exception to this.\(^{3,52}\) Therefore, the dye adsorption on the surface of the photocatalyst is crucial in photocatalysis in addition to other factors such as creation of electron–hole (e\(^{-}\)–h\(^{+}\)) pairs on photoxeitation and generation of reactive oxygen species (ROS), followed by oxidative degradation of the dye on the action of ROS. In most cases, the photogenerated conduction band (CB) electrons are transferred to the adsorbed oxygens to yield superoxide radical anions (O\(_2^{•−}\)) and the VB holes oxidize adsorbed water molecules to produce *OH radicals, which further take part in the dye degradation. Moreover, the photogenerated VB holes on the semiconductors may also oxidize the adsorbed dyes into CO\(_2\) and H\(_2\)O. However, the actual mechanism in a photocatalytic degradation can be understood based on the relative positioning of the semiconductor VB and CB potentials with respect to the potentials of \*OH/H\(_2\)O, O\(_2^-\)/O\(_2\)\(^{•−}\), and the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) levels of the degrading molecule.

To explain the photocatalytic mechanism, an energy level diagram (ELD) is constructed. For this, the relative band edge positions of the photocatalysts were calculated using the following empirical formulas:\(^{51}\)

\[
E_{CB} = \chi(A_0, B_0, C_0) - 1/2E_g + E_0
\]

\[
E_{VB} = E_{CB} + E_g
\]

Using the above equations, the CB and VB positions (E\(_{CB}\) and E\(_{VB}\)) of Bi\(_5\)ATi\(_4\)FeO\(_{18}\) (A = Ca, Sr, and Pb) are calculated and summarized in Table 3. The potentials for the generation of *OH \([E_{OH/H_2O} = +2.68\ eV vs normal hydrogen electrode (NHE)]\) and O\(_2^{•−}\) \([E_{O_2^{•−}/O_2} = +0.13\ eV vs NHE]\) radicals and the HOMO–LUMO levels of the dyes (RhB and MB).

2.10. Role of Adsorption and ζ-Potential. On the basis of our earlier reports,\(^{3,52}\) dye adsorption being a crucial factor for enhanced photocatalysis, it was intriguing to investigate into the photocatalytic selectivity based on adsorption. Interestingly, the adsorption results (Figure 15) in mixed dye solutions indicated selective adsorption of MB in neutral and alkaline media for all the catalysts. However, it shows both MB and RhB adsorption to comparable extents in the acidic medium. The maximum adsorption of MB took place in the alkaline medium for all the catalysts. These results are consistent with selective degradation of MB in neutral and alkaline media but collective dye degradation (both MB and RhB) in the acidic medium. A faster selective degradation of MB in the alkaline medium can be attributed to its superior adsorption at pH 11, resulting in enhanced photocatalytic degradation in addition to its base-catalyzed photolysis. Moreover, the photocatalytic activity toward individual dyes also follows the adsorption order (Figure S14 in the Supporting Information), making Bi\(_5\)SrTi\(_4\)FeO\(_{18}\) as the most active catalyst, and the activity decreases in the order: Bi\(_5\)SrTi\(_4\)FeO\(_{18}\) > Bi\(_5\)PbTi\(_4\)FeO\(_{18}\) > Bi\(_5\)CaTi\(_4\)FeO\(_{18}\).

The catalyst surface charge plays a vital role in the dye adsorption process. Therefore, to probe the surface charge of the catalysts, the ζ-potentials were measured at different pHs. The highest negative ζ-potentials are observed at pH 13 (Figure 15d). As the pH is decreased, the ζ-potential decreases from more negative potentials to less negative potentials, and finally, it becomes positive in the acidic medium. This trend is
mostly due to the action of H⁺ and OH⁻ ions on the surface hydroxyl groups of the oxide.32

Interestingly, the ζ-potential of the catalysts is mirrored in the selective dye adsorption. At pH 11, the highest selective MB adsorption takes place on Bi₅SrTi₄FeO₁₈, which has the highest negative ζ-potential (−55.1 mV) as compared to Bi₅PbTi₄FeO₁₈ and Bi₅CaTi₄FeO₁₈ with ζ-potentials of −50.1 and −48.2 mV, respectively. Moreover, the selective MB adsorption to a moderate extent is also noticed at pH 7. This has also been attributed to the negative ζ-potentials of the catalysts at this pH. The pronounced adsorption of MB in neutral and alkaline media is believed to be due to the electrostatic attraction of negatively charged catalyst surfaces with the cationic MB molecules, whereas a negligible adsorption of RhB is attributed to the electrostatic repulsion between the negatively charged carboxylic acid groups of RhB with the negatively charged catalyst surface. Being zwitterionic in nature, an electrostatic attraction of the positively charged N-diethyl end of RhB with the negatively charged surface may also be considered, but it will not result in any favorable adsorption.32 However, it is interesting to observe that all the compounds reported here show adsorption of MB, RhB, and Rh6G in the acidic medium (Figure S14 in the Supporting Information). The higher adsorption of RhB in the acidic medium from the RhB/Rh6G mixture can be understood from previous reports,32 whereas a lower adsorption of Rh6G can be attributed to the weaker electrostatic attraction because of the presence of the bulky −OC₂H₅ group in place of the carboxylate (see Figure S15 in the Supporting Information). The highest adsorption of RhB and MB takes place over Bi₅SrTi₄FeO₁₈, which acquires the most positive ζ-potential (+39.7 mV) among the catalysts at pH 2. The ζ-potentials for Bi₅PbTi₄FeO₁₈ and Bi₅CaTi₄FeO₁₈ are +34.1 and +29.8 mV, respectively. Although the adsorption of MB (a cationic dye) at pH 2 appears unusual on a positively charged catalyst surface, it may probably be due to the favorable electrostatic interaction of the lone pair of nitrogen-rich moieties (basic) with the surface hydroxyl protons (acidic) of the catalyst.

The rate of individual MB degradation is faster than that of selective degradation in the presence of RhB at pH 11. It is evident from the ELD that the energy level positioning of RhB is suitable for the dye sensitization mechanism to be operative in these catalysts and expected to enhance the rate of degradation. This apparent contradiction, however, supports the adsorption-based mechanism where the principle route to degradation is through h⁺ transfer from the semiconductor VB to the adsorbed dye molecule. The zeta-potential-mediated adsorption selectivity results in an enhanced MB adsorption at pH 11, whereas the RhB adsorption is almost negligible, thus making the photosensitization by electron transfer from RhB to the semiconductor CB insignificant. On the other hand, RhB, being a strong absorber of the visible light and having an overlap of its absorption band with the band edge of the semiconductors, only allows a part of the incident light for semiconductor excitation in addition to reducing it gradually up to the bottom of the dye–catalyst suspension to a considerable extent. It is believed that this combined effect makes the selective MB degradation rate slower as compared to that of the individual dye at pH 11. Moreover, it is concluded that the near 100% selectivity of MB degradation in the presence of RhB at pH 11 is not only due to its preferential adsorption but also due to an h⁺-specific degradation pathway together with its base-catalyzed photolysis. Otherwise, both dyes would have degraded to significant extents in the alkaline media, had the generated ROS (O₂•− and "OH) instead of h⁺ been the dominant species for degradation.

Last, a correlation of crystal chemistry of the Aurivillius phases with their catalytic activity is in order. All the compounds under discussion crystallize in a noncentrosymmetric space group (F2mm) belonging to a polar crystal class. The crystal structure is likely to influence their electric polarization properties, which in turn would influence the catalyst surface charge. To analyze and understand any role of

Figure 15. Influence of pH on the preferential adsorption of dye from aqueous mixtures of MB and RhB on (a) Bi₅CaTi₄FeO₁₈, (b) Bi₅SrTi₄FeO₁₈, and (c) Bi₅PbTi₄FeO₁₈. (d) ζ-potential of Bi₅ATi₄FeO₁₈ (A = Ca, Sr, and Pb) catalysts at different pHs.
crystal structure on the varied extent of adsorption and photocatalytic activity, the octahedral distortion parameter $\Delta_o$ for the Ti/FeO$_6$ octahedra of all the compounds is calculated (Figure S16 and Table S3 in the Supporting Information). The calculated $\Delta_o$ values for the terminal octahedra differ to a considerable extent from Ca, Sr, to Pb analogues having the highest $\Delta_o$ of 0.011 for the Ca compound and smaller $\Delta_o$ values of 0.005 and 0.008 for Pb and Sr, respectively. Moreover, the $\Delta_o$ values gradually decrease in the order: terminal > preterminal > central octahedra for any given compound. This is consistent with the second-order Jahn–Teller (SOJT) distortion trends observed in other series of layered perovskites, where the terminal layer is distorted to the highest extent and it gradually decreases as one proceeds toward the central layer. It is found that the activity order is not consistent with the order of the calculated $\Delta_o$ values. To have further insights into the nature of Aurivillius perovskite surfaces and effects of local octahedral distortion on the adsorption phenomena, the axial distortion parameters ($\Delta_{ax}$) for the octahedra are calculated considering only the distortion of the axial bonds arising out of the SOJT effect. The axial distortion parameter is defined as $\Delta_{ax} = \frac{1}{2} \sum_i (l_i - \bar{l})/\bar{l}$, where $l_i$ are axial bond lengths parallel to the crystallographic c-axis and $\bar{l}$ is the average bond length of the octahedra. Interestingly, the variation of $\Delta_{ax}$ across the octahedral layers for any given compound also follows the order of distortion similar to $\Delta_o$ being highest for the terminal and lowest in the central octahedral layer. Moreover, the $\Delta_{ax}$ for the terminal octahedral layer of the Sr analogue is the highest and decreases in the order: Sr > Pb > Ca (see Table S3 in the Supporting Information). This is mirrored in the order of catalyst surface charge (Figure 15d), dye adsorption, and subsequently in the photocatalytic activity order is manifested because of compositional modifications at the A-sites of the perovskites mainly by alkali and alkaline earth metals.

3. CONCLUSIONS

Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb), a new series of five-layer Aurivillius perovskites, was synthesized and reported for the first time. All the compounds crystallized in an orthorhombic structure with Fe largely occupying the central octahedral perovskite layer. The compounds have shown excellent selective solar photocatalysis in MB degradation from an aqueous RhB–MB mixture at pH 11. While the rate of selective MB degradation decreased at pH 7, the catalysts showed collective degradation of MB and RhB at pH 2. The photocatalytic activity studies established Bi$_5$SrTi$_4$FeO$_{18}$ as the most active catalyst among all the Aurivillius oxides reported here. Scavenger tests with Bi$_5$SrTi$_4$FeO$_{18}$ indicated h$^+$ and O$_2$$^-$$^*$ as the major reactive species contributing toward photocatalytic RhB and MB degradations. The empirical ELD is supportive of the h$^+$- and O$_2$$^-$$^*$-mediated photocatalytic dye degradations. The photocatalytic cycle tests and postcatalytic P-XRD analysis confirmed the cyclability and excellent stability of the catalysts in a wide pH range. The enhanced photocatalytic activity of Bi$_5$SrTi$_4$FeO$_{18}$ as compared to that of the Ca and Pb analogues corroborated well with an enhanced dye adsorption that occurred possibly due to an enhanced electric polarization arising out of axial octahedral distortion of SOJT origin. The selective solar photocatalysis demonstrated here is appealing for the development of new catalysts that are selective and harvest solar light for environmental remediation purposes. This may also unlock new possibilities for recovery or purification of precious dyestuffs and chemicals from a mixed solution of pollutants, wastes, and byproduct mixture through selective solar photocatalysis. Moreover, the role of axial octahedral distortion ($\Delta_{ax}$) may work as an indicator for the tolerance factor-based cationic and anionic manipulations for the exploration of a large number of photocatalysts in homologous series and better design of improved catalytic systems based on structural principles.

4. EXPERIMENTAL SECTION

4.1. Materials and Synthesis. Bi$_5$O$_3$ (≥98%), CaCO$_3$ (≥99.9%), SrCO$_3$ (≥99.9%), PbCO$_3$ (≥99.9%), TiO$_2$ (99.8%), and FeC$_2$O$_4$·2H$_2$O (99%) were purchased from Sigma-Aldrich and used as received. The other reagents employed in our experiments were of analytical grade and used without any further purification. All the dye solutions were freshly prepared before the experiments in Millipore (Bedford, MA, USA) water.

Polycrystalline samples of Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb) were prepared by solid-state reactions. For this, stoichiometric quantities of Bi$_2$O$_3$, ACO$_3$ (A = Ca and Sr)/PbO, TiO$_2$, and FeC$_2$O$_4$·2H$_2$O were thoroughly ground in an agate mortar for 1 h and heated at 780 °C for 2 h. Afterward, the powders obtained after initial heating were reground, pelletized, and heated at 1000 °C for 2 h.

4.2. Characterization. The progress of the reaction and phase purity of the resulting products were monitored by P-XRD recorded on a Bruker AXS D8 ADVANCE diffractometer using graphite monochromatized Cu Kα ($\lambda = 1.5406$ Å) radiation in the range 5° ≤ θ ≤ 90° with a step size of 0.018°. Unit cell parameters of the samples were least-squares refined using the PROSIZKI program. Rietveld refinement of the P-XRD data for Bi$_5$ATi$_4$FeO$_{18}$ (A = Ca, Sr, and Pb) was carried out using the FullProf program suite. For refinements, the P-XRD data were collected in the 10–90° angular range at 40 kV and 30 mA with a data collection time of 6 h and a step size of 0.018°. In the initial refinement runs, the background coefficients along with zero-shift and cell parameters were refined. In the subsequent runs, the profile and shape parameters were refined. In case, where the program diverged, the profile and shape parameters were refined one by one. The positional and thermal parameters were refined in the later stages of the refinement by systematically starting with heavier atoms first and then subsequently moving to those of the lighter atoms. Moreover, to avoid divergence, the thermal parameters of oxygens were fixed to the value reported for the model system. Finally, the cation disorder was examined by using the refined position and thermal parameters and refining the varying occupancy of the atoms.

Microstructural studies of the as-prepared compounds were carried out using FE-SEM (Zeiss FE-SEM, Ultra Plus S5), operating at an accelerating voltage of 20 kV. Qualitative and
quantitative elemental analysis and elemental mapping of the compounds were carried out using an EDS facility (Oxford Instruments) attached with the FE-SEM instrument. Transmission electron microscopy (TEM) images and SAED patterns were recorded with a FEI Tecnai G² microscope, operated at an acceleration voltage of 200 kV.

UV–vis DRS were recorded on a Shimadzu UV-2450 UV–vis spectrophotometer in the 200–800 nm wavelength range using BaSO₄ as a reference material. The band gap of the semiconductors was estimated employing standard procedures and equations⁶³–⁶⁵ as described in the Supporting Information.

The PL spectra of the compounds were recorded in a Shimadzu RF-5301PC spectrofluorophotometer in the wavelength range of 400–650 nm with an excitation wavelength of 350 nm. The surface charge of the semiconductor catalyst particles was measured on Zetasizer Nano ZS90 from Malvern Instruments, UK, in water suspensions of appropriate pH.

XPS analysis was carried out using a Physical Electronics PHI 5000 VersaProbe III spectrometer (Physical Electronics) using Al Kα radiation (1486.6 eV).

4.3. Adsorption Test. Adsorption tests were carried out for individual RhB, MB, and Rh6G at pH 2 solutions together with a mixed solution of RhB and MB at different pHs in the dark. For this, 50 mg of Bi₅ATi₄FeO₁₈ (A = Ca, Sr, and Pb) (as the adsorbent) was dispersed in 50 mL of 1 × 10⁻⁵ M dye solution at appropriate pH (2, 7, and 11). For the mixed dye adsorption experiment, 25 mL each of RhB and MB of 2 × 10⁻⁵ M concentration was mixed to maintain the same catalyst to the individual dye concentration. After stirring at 350 rpm for 6 h in the dark, the suspensions were centrifuged and a portion of the centrifugate was used for absorption measurements on a Shimadzu 2450 UV–vis spectrophotometer. The percentage of dye adsorption was calculated using the following expression.

\[
\text{Adsorption (\%) = } \left(1 - \frac{C}{C_0}\right) \times 100
\]

where C is the concentration of the dye after 6 h stirring and \(C_0\) is the initial dye concentration.

4.4. Photocatalysis. The photocatalytic dye degradation studies were carried out with individual RhB, MB, and a mixture of RhB–Rh6G at pH 2 and RhB–MB under sunlight irradiation at different pHs (2, 7, and 11). All the photocatalytic experiments were carried out at IIT Roorkee (29°51’ N; 77°53’ E) under similar conditions in the month of October–November under full sunlight irradiation (solar direct normal irradiance ≈216–142 W/m²). For this, 0.1 g of the catalysts (optimized by the dosage test, see the Supporting Information), Bi₅ATi₄FeO₁₈ (A = Ca, Sr, and Pb), was suspended in 100 mL of 1 × 10⁻⁵ M dye solution of appropriate pH. Prior to irradiation, the catalyst–dye suspensions were magnetically stirred for 1 h in the dark to ensure the establishment of adsorption–desorption equilibrium between the catalyst and dye molecules. For monitoring the dye degradation with time, an aliquot (~3 mL) from the dye–catalyst suspension was periodically sampled and centrifuged at 8200 rpm (to remove the catalyst particles) for absorbance measurements on a Shimadzu 2450 UV–vis spectrophotometer. A blank control experiment was always performed using the same dye solution under study in the absence of catalysts in an identical experimental condition.

The photocatalytic degradation kinetics over Bi₅ATi₄FeO₁₈ (A = Ca, Sr, and Pb) were fitted with the Langmuir–Hinshelwood model

\[
\ln(C_0/C) = kt
\]

where \(C_0\) is the initial dye concentration, C is the concentration of dye at time t, and k is the rate constant. The linearity of \(\ln(C_0/C)\) versus irradiation time plots affirmed the pseudo-first-order nature for the kinetics of dye degradation reported here. Photocatalytic cycle tests were performed using the same procedures as described in our earlier studies.⁶²

4.5. Analysis of Reactive Species. To understand the role of the reactive species for the degradation of RhB or MB over Bi₅SrTi₄FeO₁₈ under sunlight irradiation, appropriate scavengers were added into the RhB or MB solution, and the degradation experiments were carried out in a similar fashion to those described in photocatalysis studies. In these experiments, AO, BQ, and tertiary butyl alcohol (t-BuOH) were used as scavengers for holes (h+), superoxide radical anions (O₂⁻⁻), and hydroxyl radicals (·OH), respectively.

To confirm the generation of hydroxyl radicals (·OH) in MB dye solution at pH 11 under sunlight irradiation, PL experiments were carried out using TA as a probe molecule. For this, 0.0083 g of TA powder was dissolved in 100 mL of 10⁻⁵ M aqueous MB solution of pH 11 (adjusted with NaOH), and the solution was magnetically stirred in the dark for 60 min before irradiating it to the sunlight. The PL spectra were recorded on aliquots withdrawn at regular time intervals by a fluorescence spectrophotometer at an excitation wavelength of 315 nm. Similar experiment was also performed in the dark as a reference blank test.

4.6. COD Test. Mineralization of the dyes during and after photocatalysis was monitored by using a digestion unit (DRB 200, HACH, USA) and a UV–visible spectrophotometer. For this, multiple degradation experiments were carried out with the same set of dyes and catalysts. The dye–catalyst suspensions were exposed to sunlight for different time intervals, and the aliquots were collected for COD analysis. The photodegradation efficiency was calculated by using the following equation.

\[
\text{Photodegradation efficiency} = \frac{\text{initial COD} - \text{final COD}}{\text{initial COD}} \times 100
\]
degradation over Bi₂SrTi₄FeO₁₈, cycle test for MB degradation by Bi₂SrTi₄FeO₁₈ at pH 11; P-XRD patterns of Bi₂₄Ti₃FeO₁₈ (A = Ca and Pb) after photocatalysis; adsorption of RhB and MB at different pHs and Rh6G at pH 2 over Bi₂₄Ti₃FeO₁₈ (A = Ca, Sr, and Pb); structures of MB, RhB, and Rh6G; structure with axial and equatorial bond distances for the terminal, preterminal, and central octahedra of Bi₂₄Ti₃FeO₁₈ (A = Ca, Sr, and Pb); and octahedral distortion parameters (PDF)

### ACKNOWLEDGMENTS

The authors declare no competing financial interest.

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