Research Article

Ana Sofia Rodrigues*, Maria Estrela Melo Jorge, Lurdes Ciríaco, Maria José Pacheco, and Ana Lopes

Perovskites (La,Ba)(Fe,Ti)O₃: AO7 photocatalysis under visible light

<https://doi.org/10.1515/rams-2020-0012>

Received Sep 11, 2019; accepted Jan 02, 2020

Abstract: Perovskites BaTiO₃, La_{0.1}Ba_{0.9}TiO₃ and BaFeO₃ were prepared by different methods and utilized as photocatalytic material for the degradation of the AO7 dye, with visible light. The toxicity of the treated solutions and the toxicity of perovskite powders that remained in suspension after centrifuged was assessed.

Different catalytic properties were found by changing synthesis methods, annealing conditions, temperature of assay, initial concentration of pollutant and amount of perovskite in suspension. BaTiO₃ was prepared by ceramic or complex polymerization methods. This perovskite presents cubic structure, and the preparation method do not seem to have any influence on the unit cell parameter. On the other hand, annealing temperature has a marked influence on the time needed to attain good crystallinity. In the case of BaFeO₃ prepared by the ceramic method, for low annealing temperature there is the formation of tetragonal phase, which changes to hexagonal with the increase in annealing temperature, being a Ba₂Fe₂O₅ monoclinic phase involved in this phase transition.

Regarding AO7 photocatalytic degradation, the best results, with almost complete colour removal, were obtained with BaFeO₃ (97%), prepared by ceramic method, and with BaTiO₃ (78%), prepared by polymer complex method. Toxicity assays towards *Daphnia magna* were performed with AO7 25 ppm aqueous solution samples, collected in the centrifuged suspensions of the photocatalytic assays, performed with different perovskites, and samples collected in centrifuged suspensions of perovskite powders. In general, there is no increase in toxicity when compared

to the toxicity of an AO7 25 ppm aqueous solution. Only in the photodegradation assay with BaFeO₃ a clear increase in toxicity was observed, indicating that toxic by-products are being formed.

Keywords: Perovskites, Photocatalysis, Visible Light, AO7, (La,Ba)(Fe,Ti)O₃ Synthesis

1 Introduction

Photocatalysis is an important process for environmental applications, in particular when the photocatalytic materials are activated by a clean energy, such as visible or solar light. One of the groups of photocatalytic materials that may be activated by visible light are the metal oxides with perovskite structure.

Perovskites are a class of compounds presenting the general formula ABX₃, where A is an alkali or alkaline earth metal or a member of the lanthanides' family, B is a transition metal, X is an anion, frequently an oxygen ion. Their structures offer a rich opportunity for designing novel compounds based on A and B site occupancy, giving rise to a wide range of material systems with unique properties [1]. Due to their structure, perovskite oxides can accommodate about 90% of the Periodic Table metal elements, which may partially or fully occupy the A and/or B positions without destroying the matrix structure, but giving them different catalytic properties [2]. The partial substitution of the cation sites (A or B) with other cations (A' or B') results in A_xA'_{1-x}B_yB'_{1-y}O_{3-δ} compounds [3]. Most of the perovskites with titanium in B position present band gap energy (E_g) values higher than 3.0 eV, showing excellent photocatalytic properties under UV radiation. However, doping may be used to change their optical properties, inducing visible light absorption [1]. FeTiO₃ and LaFeO₃, with E_g of 2.8 and 2.1 eV, respectively, may absorb visible light [1, 4]. Thus, the choice of suitable elements for sites A and B that confers adequate photocatalytic properties to the perovskite oxide may be an interesting challenge. Different morphologies and surface properties may

*Corresponding Author: Ana Sofia Rodrigues: FibEnTech-UBI, Universidade da Beira Interior, 6201-001 Covilhã, Portugal; Email: ana.sf.rodrigues@ubi.pt; Tel.: +351 275 241 329

Maria Estrela Melo Jorge: Centro de Química e Bioquímica and BioISI, Biosystems and Integrative Sciences, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

Lurdes Ciríaco, Maria José Pacheco, Ana Lopes: FibEnTech-UBI, Universidade da Beira Interior, 6201-001 Covilhã, Portugal

also play an important role on the photocatalytic activity of the materials [5].

Some perovskites have already been tested as photocatalysts under visible-light for dyes degradation: LaFeO₃ nanostructures with Rhodamine B [6]; Ca-doped BiFeO₃ nanofibers with Congo Red [7]; (CH₃NH₃)₃Bi₂I₉ with a fluorone dye, Rhodamine B, a thiazine dye, methylene blue, and an azo dye, reactive Blue 4 [8]. Other studies described the use of perovskites under sunlight or simulated solar light: Sr_{0.85}Ce_{0.15}FeO_{3-δ} as catalyst for Orange II and Rhodamine B degradation [9]; LaFeO₃ and LaFe_{0.9}Mn_{0.1}O_{3-δ} in the photocatalytic degradation of methyl orange [10]; AlFeO₃/TiO₂ nanocomposite for the photodegradation of methyl orange and eosin [11], β-AgVO₃ for photocatalytic degradation of Rhodamine B dye [12].

Azo dyes are well known for their bio-recalcitrant and acute toxicity, since they are being continuously introduced into the aquatic environment through various anthropogenic inputs [13]. An example is Acid Orange 7 (AO7), an azo dye that can be partially biodegraded by anaerobic treatment to give, by reduction of the azo bond, the by-products sulfanilic acid (SA) and 1-amino-2-naphthol (AN) that can be very harmful to the environment, especially AN, an unstable aromatic amine [14]. Thus, the aim of this work was to prepare mixed metallic oxides of the perovskite family La_xBa_(1-x)Fe_yTi_(1-y)O₃, synthesized by ceramic or polymerization complex methods, at different annealing conditions, and evaluate their photocatalytic activity in suspension for the degradation of the azo dye AO7, and evaluate the toxicity of the treated solutions.

2 Experimental

Mixed metallic oxides of the perovskite family La_xBa_(1-x)Fe_yTi_(1-y)O₃, namely BaTiO₃, BaFeO₃ and La_{0.1}Ba_{0.9}TiO₃, were prepared utilizing the ceramic method [15]. For their synthesis, stoichiometric amounts of commercial La₂O₃ (Acros Organics, +99.9%), BaCO₃ (Fluka, +99.0%), Fe₂O₃ (Merk, +99.0%) and TiO₂ (Aldrich, +99.8%) were weighed, milled for 30 min, pre-calcined at 900°C in a tubular furnace, for 6 h, and calcined at 1130°C, for 4 h. To study the influence of the calcination time on the perovskite properties, the calcined mixture was milled for 15 min and divided into several parts that were subjected to extra calcination periods, at 1130°C. Besides the consecutive heating, BaFeO₃ was also calcinated at 1200°C for 4 h, to study the influence of calcination temperature on the perovskite's properties. After each heating step of the

perovskite preparation, a sample was collected to perform X-ray analysis.

The perovskites BaTiO₃ and BaFeO₃ were also synthesized by the complex polymerization method (adapted from [16,17]) using stoichiometric amounts of commercial BaCO₃ (Fluka, +99%), C₁₂H₂₈O₄Ti (Acros Org., +98%) and FeN₃O₉·9H₂O (Sigma-Aldrich, 99.95%). For the BaTiO₃ preparation, C₁₂H₂₈O₄Ti, after weighed, was first dissolved in ethylene glycol (Carlo Erba, +99.5%), and then citric acid (Aldrich, +99%) was added, being ethylene glycol/citric acid volumetric ratio 1:4. BaCO₃ was then added and the resulting mixture was submitted to successive heating: first at 50°C, with stirring, until the solution becomes clear; then at 90°C, until a gel is formed; to complete the polymerization, i.e., formation of a dark resin, at 150°C for 20 minutes; finally, at 400°C, for 2 h, in a tubular furnace, with a heating speed of 5°C/min, for the formation of a black precursor powder. After cooling, the powder was withdrawn from the furnace and weighed, and then calcined at 900°C, for 3 h (5°C/min), cooled, weighed again, milled for 15 min, calcined again at 900°C, for 3 h (5°C/min), cooled and milled again for 15 min. After each step of the perovskite preparation, a sample was collected to perform X-ray analysis. The preparation of BaFeO₃ by the complex polymerization method was like that of BaTiO₃, being the only difference the utilization of FeN₃O₉·9H₂O instead of C₁₂H₂₈O₄Ti.

All the synthesized powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and dispersive energy spectroscopy (EDS). Perovskite X-ray diffraction analysis was performed using a Rigaku diffractometer, model DMAX III/C with automatic data acquisition (APD Philips v3.5B), equipped with a monochromatized Cu Kα radiation (λ = 0.15406 nm), operating at 40 mA and 30 kV. Crystallites' dimension was calculated by means of Scherrer equation. SEM and EDS characterization were performed in a Hitachi (S-2700)/Oxford (60–74) system operating at 20 keV. The diffuse reflectance spectra of the perovskite films were obtained in an UV-Vis spectrometer Shimadzu UV-2600PC, equipped with an integrating sphere ISR 2600plus, over the spectral range 200–800 nm. BaSO₄ was utilized as reflectance standard and Kubelka-Munk function was used to analyze the diffuse reflectance spectra.

A new setup (Figure 1) was used to test several perovskites powders in simultaneous photocatalytic degradation assays. 10 mL assays were performed in batch mode with orbital stirring for 6 h, under visible light (OSRAM, 300W). Different AO7 initial concentrations (5 to 25 ppm) were tested, at different temperatures. The influence of the amount of perovskite powders in suspension was also

Figure 1: Setup for the photocatalytic assays.

investigated (2.5 mg, 5 mg or 7.5 mg in 10 mL of pollutant solution). A07 degradation tests were monitored by UV-Vis absorption spectrophotometry (Shimatzu UV-1800 spectrophotometer) at wavelengths ranging from 200 to 800 nm.

After the photocatalytic assays, solutions were centrifuged. Some centrifuged samples collected from the assays performed with A07 25 ppm solutions were utilized for toxicity assessment, evaluated with *Daphnia magna* (Daphtoxkit MicroBioTests DM140818). Centrifuged samples of suspensions containing only perovskite powder were also utilized for toxicity assessment, to evaluate perovskite toxicity. To validate *Daphnia Magna* tests, OECD Guideline 202 (2004) recommends a test with a reference substance (such as potassium dichromate), in order to assess the sensitivity of the organisms. Five different concentrations were prepared in fresh standard water. For each replicate, 5 neonates with less than 24 h were exposed to the test solutions during 24 h and 48 h. After this exposure period, the number of immobilized daphnids was registered and the concentration responsible for 50% of immobilization (EC50) was calculated, using DAPHTOXKIT F data treatment spreadsheet.

3 Results and Discussion

Figure 2 presents the XRD patterns for some of the prepared perovskite oxides. BaTiO₃, prepared either by ceramic or complex polymerization (PC) methods (Figure 2a), presents cubic structure, with a cell parameter of approxi-

mately 0.4 nm (Table 1). The preparation method does not seem to have any influence on the unit cell. However, annealing temperature has a marked influence on the time needed to attain good crystallinity, as can be seen for the PC method that presents much better crystallinity after 2 h at 1130°C than after 6 h at 900°C. In fact, in the XRD pattern of the latter some vestigial reagents can be observed. The introduction of La (10%) in the BaTiO₃ structure, to obtain La_{0.1}Ba_{0.9}FeTiO₃, did not change the cubic structure, nor the cell parameter. These results show the importance of the annealing temperature on the time needed to attain good crystallinity.

Regarding BaTiO₃ crystallite size (Table 1), the preparation method and annealing temperature seem to have some influence on it. In fact, crystallite size is higher for PC method and increases with annealing temperature. This increase in crystallite size may present a drawback regarding the photocatalytic activity of the prepared powders, since its increase leads to a decrease in the surface area of the powders.

The XRD patterns of the BaFeO₃ powders prepared by the ceramic method (Figure 2b) show characteristic peaks of a tetragonal phase. However, the low crystallinity and the existence of small peaks that fit in the hexagonal and cubic geometries lead to the conclusion that there are also other phases present, although in smaller quantity. Keeping the annealing temperature at 1130°C and increasing the annealing time to 12 or 28 h, the tetragonal phase is still predominant, although the small peaks that fit in the hexagonal and cubic geometries are shown. The increase in the annealing time also leads to the presence of a peak at 32.2° that may be assigned to a monoclinic Ba₂Fe₂O₅ phase or to an orthorhombic BaFeO_{2.6} phase. The relative importance of this new phase increases with temperature, as can be seen when its (110) Miller index is compared to the BaFeO₃ tetragonal phase, showing also a decrease of oxygen in the unit cell with annealing time. However, when the annealing temperature is increased to 1200°C, the main phase changes to hexagonal, with a correspondence of 82% (according to PDF#23-1024), with small peaks that can be assigned to tetragonal and cubic phases. Also, the Ba₂Fe₂O₅ monoclinic phase disappears. On the other hand, if BaFeO₃ is prepared by the complex polymerization method, at 900°C, the predominant phase is cubic with a correspondence of 97% (according to PDF#14-0180), with simultaneous existence of hexagonal and tetragonal phases, but with small expression. Apparently, at low temperature there is the formation of a cubic phase that gradually changes to tetragonal, with annealing time, and to hexagonal with the increase in annealing

Table 1: Physical properties of perovskite powders prepared by different experimental conditions.

Preparation method	BaTiO ₃		La _{0.1} Ba _{0.9} TiO ₃		BaFeO ₃		
	PC*	PC*	Ceramic	Ceramic	Ceramic	Ceramic	PC*
Anneal. temp/°C and time /h	900	1130	1130	1130	1130	1200	900
Crystallite size /nm	3 + 3	2	4	4	4 + 24	4	3 + 3
Unit cell**	55.76	59.28	55.16	55.12	43.57	53.56	19.87
Cell param. /nm	a=0.4014	a=0.3999	a=0.4008	a=0.4009	Tetrag.	Hexag.	Cubic
DRX PDF# card***	74-1964	74-1964	74-1964	74-1964	a=0.4028 c=0.4145	a=0.5684 c=1.3970	a=4.005
					23-1023	23-1024	14-0180

*PC – Complex polymerization; **Determined using Holland TJB, Redfern SAT. Unicell, computer program, developed at the University of Cambridge, in 1995. *** Program / Software JADE 6 with data base.

Table 2: Band gap energies and experimental chemical formula of the perovskite powders, prepared at different experimental conditions, utilized in the photodegradation assays.

Preparation method	BaTiO ₃		La _{0.1} Ba _{0.9} TiO ₃		BaFeO ₃	
	PC*	PC*	Ceramic	Ceramic	Ceramic	Ceramic
Annealing temp/°C and time /h	900	1130	1130	1130	1130	1130
Bandgap energy /eV	3 + 3	2	4	4	4	4 + 24
Exp. formula (EDS)	3.24	3.20	3.24	3.29	3.29	3.30
	Ba _{1.00} Ti _{1.05} O _{2.94}	Ba _{0.87} Ti _{1.26} O _{2.87}	Ba _{0.85} Ti _{1.00} O _{3.15}	La _{0.08} Ba _{0.83} Ti _{1.06} O _{3.04}	Ba _{1.11} Fe _{1.07} O _{2.79}	Ba _{1.13} Fe _{1.16} O _{2.72}

*PC – Complex polymerization;

Figure 2: X-Ray diffraction patterns obtained with different synthesis methods and annealing conditions for the different perovskite powders: a) $\text{La}_x\text{Ba}_{(1-x)}\text{TiO}_3$; b) BaFeO_3 .

temperature, being a $\text{Ba}_2\text{Fe}_2\text{O}_5$ monoclinic phase involved in this phase transition.

BaFeO_3 synthesis conditions also lead to changes in the crystallite size (Table 1), which increase with annealing temperature. The annealing time also increases the crystallite size and the cell parameters.

Some of the prepared perovskite powders were chosen to perform photocatalytic degradation assays of A07 aqueous solutions. Band gap values obtained for these perovskites are presented in Table 2. The respective absorption spectra are presented as supplementary material (Figure S1). All perovskites present band gap values higher than 3.2 eV, indicating that photocatalysis are mainly activated by UV light. However, they were tested with visible light, to study the possible application of these materials with solar light.

Results obtained in the photocatalytic assays with the different prepared perovskites are presented in Figure 3. It can be observed that, in general, an increase in the annealing time decreases the photocatalytic performance of the perovskites, probably because the crystallites' size increases with the annealing time (Figure 3a). An exception is observed for BaTiO_3 prepared by the ceramic method, being the absorbance removal for the powder prepared by annealing at 1130°C for 4+24 h higher than that obtained for BaTiO_3 annealed at 1130°C for 4 h. However, posterior annealing decreases the catalytic activity. These results are probably due to a balance between crystallinity and crystal size. This shows the importance of the preparing experimental conditions, such as synthesis method and annealing conditions, in the catalytic properties of the synthesized materials. With the increase in the annealing time of the BaFeO_3 preparation, there is a decrease in its absorbance removal ability for A07 at 484 nm, perhaps due to the formation of the secondary phase evidenced in the XRD pattern and/ or the increase in the crystallites' dimension.

For the best photocatalytic degradation results obtained with 500 ppm perovskite suspensions, different amounts of perovskite powders were tested (Figure 3b). Perovskite amount does not present any influence for $\text{La}_{0.1}\text{Ba}_{0.9}\text{TiO}_3$, but an increase in the BaFeO_3 or BaTiO_3 amount increases the absorbance removal at 484 nm of the A07 solution at 6 h degradation time. The best results were attained with BaTiO_3 . These results can be partially explained by the crystallite size.

Assay temperature (Figure 3c) has a small influence on the BaTiO_3 and $\text{La}_{0.1}\text{Ba}_{0.9}\text{TiO}_3$ catalytic performance, but, for BaFeO_3 the increase in temperature increases the photocatalytic performance. This different behaviors must

Figure 3: Influence on the absorbance removal of (a) the type of perovskite, (b) perovskite concentration and (c) temperature for the assays performed with AO7 5 ppm solutions and (d) AO7 removal for different initial AO7 concentration, for the photocatalytic degradation assays. Cer – Ceramic method; PC – Complex polymerization method.

be related with adsorption/desorption thermodynamics of the different perovskites.

In general, the amount of AO7 removed increases with its initial concentration (Figure 3d). However, for higher AO7 initial concentration studied (20 and 25 ppm) there is a stabilization in AO7 removal with BaTiO₃ and La_{0.1}Ba_{0.9}TiO₃.

Results from the toxicity assessment of an AO7 25 ppm aqueous solution, the samples collected in the centrifuged suspensions of the photocatalytic assays performed with different perovskites, and in the centrifuged suspensions prepared only with the perovskites are presented in Figure 4 as 48 h EC₅₀. 24 h EC₅₀ were also determined and they are very similar to those obtained at 48 h. When the toxicity results are compared with that from the AO7 25 ppm aqueous solution, the following conclusions may be drawn: The most toxic degradation products were obtained in the

assay performed with BaFeO₃, and, since the toxicity of the centrifuged suspension of the photocatalytic assay is higher than that of the centrifuged suspension prepared only with BaFeO₃ (i.e., lower 48 h EC₅₀), this increase in toxicity must be mainly due to the by-products of the AO7 photodegradation; In the case of BaTiO₃, neither the perovskite nanopowders that may remain in suspension nor the photodegradation by-products led to any increase in toxicity when compared to the initial AO7 solution; For La_{0.1}Ba_{0.9}TiO₃, there is a slight increase in toxicity, equal for the final suspensions of the photodegradation assay and of the perovskite alone, indicating that this small increase must be due to the presence of the perovskite crystallites.

Figure 5 presents the UV-Visible absorption spectra obtained for the samples collected at 6 h of the photocatalytic assays performed with AO7 5 ppm aqueous solutions utiliz-

Figure 4: Results of the toxicity assays performed with an A07 25 ppm aqueous solution and with the supernatant of the centrifuged suspensions of the A07 photocatalytic assays and with the centrifuged suspensions prepared with the different perovskites.

ing 500 ppm suspensions of different perovskites, besides a blank 6h-assay of photolysis. It suggests different degradation mechanisms associate with the photocatalytic activity of the perovskites utilized. Regarding photolysis with visible light, there is no A07 degradation and spectrum remains unchanged during the assay. This was expected since this dye is supposed to be stable under visible light. In the assays performed with La_{0.1}Ba_{0.9}TiO₃, there is a regular reduction in absorbance at all wavelength, pointing to a non-specific degradation mechanism that attacks the molecule in different places, leading to its complete combustion, *i.e.*, conversion to inorganics such as water, carbon dioxide and inorganic nitrogen forms. This is often obtained by indirect degradation mechanisms, intermediated by hydroxyl radicals, for instance. Regarding the assays performed with BaFeO₃ and BaTiO₃, the first bond to be broken is the azo bond, which absorbs at 484 nm. This leads to the formation of smaller organic molecules, such as sulfanilic acid (characteristic peak at 252 nm) and 2-amino-naftol. This may suggest a degradation mechanism mainly due to adsorption on the perovskite surface that leads to conversion by direct oxidation. The difference in the degradation rate at BaFeO₃ and BaTiO₃ must be due to the difference in the crystallite size, which is smaller for BaFeO₃ with the consequent increase in surface area.

Figure 5: UV-Vis. Absorption spectra of the final solutions of the photocatalytic 6h-degradation assays performed with A07 5 ppm aqueous solutions utilizing 500 ppm suspensions of different perovskites.

4 Conclusions

La_xBa_(1-x)Fe_yTi_(1-y)O₃ perovskites may be efficient photocatalytic materials for environmental applications activated by visible light. The perovskite stoichiometry and the synthesis method may result in different photocatalytic abilities. The best A07 degradation results, with almost complete color removal, were obtained with BaTiO₃ (78% at 23°C), prepared by polymer complex method, with a shorter annealing time, and with BaFeO₃ (97% at 35°C), prepared by the ceramic method, showing that the catalytic performance of the perovskites La_xBa_(1-x)Fe_yTi_(1-y)O₃ changes with perovskite stoichiometry. The results also show that a variation in the assay temperature may present an important contribution on the photocatalytic performance, changing the degradation rate. For some perovskites, an increase in the annealing time increases the photocatalytic capacity of the powders. Toxicity tests run with the organism *Daphnia magna* showed that perovskite powders that remain in solution/suspension after the photocatalytic assays, even after suspensions being centrifuged, do not significantly increase the toxicity. However, in the photodegradation assay with BaFeO₃ an increase in toxicity was observed, indicating that toxic by-products are being formed.

Acknowledgement: The authors thank Fundação para a Ciência e a Tecnologia, FCT, for the funding of FibEnTech-UBI, project UID/Multi/00195/2013 and for the grant SFRH/BD/109901/2015 awarded to A.S. Rodrigues.

References

- [1] Kanhere, P., and Z. Chen. A review on visible light active perovskite-based photocatalysts. *Molecules (Basel, Switzerland)*, Vol. 19, No. 12, 2014, pp. 19995–20022.
- [2] Zhu, J., H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao, and J. Li. Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis. *ACS Catalysis*, Vol. 4, No. 9, 2014, pp. 2917–2940.
- [3] Chen, H., J. Motuzas, W. Martens, and J. Costa. Degradation of azo dye Orange II under dark ambient conditions by calcium strontium copper perovskite. *Applied Catalysis B: Environmental*, Vol. 221, 2018, pp. 691–700.
- [4] Chen, T., J. Meng, S. Wu, J. Pei, Q. Lin, X. Wei, J. Li, and Z. Zhang. Room temperature synthesized BaTiO₃ for photocatalytic hydrogen evolution. *Journal of Alloys and Compounds*, Vol. 754, 2018, pp. 184–189.
- [5] Grabowska, E. Selected perovskite oxides: Characterization, preparation and photocatalytic properties—A review. *Applied Catalysis B: Environmental*, Vol. 186, 2016, pp. 97–126.
- [6] Thirumalairajan, S., K. Girija, N. Y. Hebalkar, D. Mangalaraj, C. Viswanathan, and N. Ponpandian. Shape evolution of perovskite LaFeO₃ nanostructures: a systematic investigation of growth mechanism, properties and morphology dependent photocatalytic activities. *RSC advances*, Vol. 3, No. 20, 2013, pp. 7549–7561.
- [7] Feng, Y.-N., H.-C. Wang, Y.-D. Luo, Y. Shen, and Y.-H. Lin. Ferromagnetic and photocatalytic behaviors observed in Ca-doped BiFeO₃ nanofibres. *Journal of Applied Physics*, Vol. 113, 2013, 146101 1–3.
- [8] Bresolin, B. M., S. B. Hammouda, and M. Sillanpää. Methylammonium iodo bismuthate perovskite (CH₃NH₃)₃Bi₂I₉ as new effective visible light-responsive photocatalyst for degradation of environment pollutants. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 376, 2019, pp. 116–126.
- [9] Tummino, M. L., E. Laurenti, F. Deganello, A. B. Prevot, and G. Magnacca. Revisiting the catalytic activity of a doped SrFeO₃ for water pollutants removal: Effect of light and temperature. *Applied Catalysis B: Environmental*, Vol. 207, 2017, pp. 174–181.
- [10] Wei, Z., Y. Wang, J.-P. Liu, C.-M. Xiao, W.-W. Zeng, and S.-B. Ye. Synthesis, magnetization, and photocatalytic activity of LaFeO₃ and LaFe_{0.9}Mn_{0.1}O_{3-δ}. *Journal of Materials Science*, Vol. 48, No. 3, 2013, pp. 1117–1126.
- [11] Yuan, Z., Y. Wang, Y. Sun, W. Jing, L. Bie, and Y. Duan. Sunlight-activated AlFeO₃/TiO₂ photocatalyst. *Science in China Series B-Chemistry*, Vol. 49, No. 1, 2006, pp. 67–74.
- [12] Xu, J., C. Hu, Y. Xi, B. Wan, C. Zhang, and Y. Zhang. Synthesis and visible light photocatalytic activity of β-AgVO₃ nanowires. *Solid State Sciences*, Vol. 14, No. 4, 2012, pp. 535–539.
- [13] Ahmed, S., M. G. Rasul, W. N. Martens, R. Brown, and M. A. Hashib. Advances in Heterogeneous Photocatalytic Degradation of Phenols and Dyes in Wastewater: A Review. *Water, Air, and Soil Pollution*, Vol. 215, No. 1–4, 2011, pp. 3–29.
- [14] Carvalho, C., A. Fernandes, A. Lopes, H. Pinheiro, and I. Gonçalves. Electrochemical degradation applied to the metabolites of Acid Orange 7 anaerobic biotreatment. *Chemosphere*, Vol. 67, No. 7, 2007, pp. 1316–1324.
- [15] Shao, S., J. Zhang, Z. Zhang, P. Zheng, M. Zhao, J. Li, and C. Wang. High piezoelectric properties and domain configuration in BaTiO₃ ceramics obtained through the solid-state reaction route. *Journal of Physics D: Applied Physics*, Vol. 41, 2008, 125408.
- [16] Vinothini, V., P. Singh, and M. Balasubramanian. Synthesis of barium titanate nanopowder using polymeric precursor method. *Ceramics International*, Vol. 32, No. 2, 2006, pp. 99–103.
- [17] Kakihana, M., T. Okubo, M. Arima, O. Uchiyama, M. Yashima, M. Yoshimura, and Y. Nakamura. Polymerized Complex Synthesis of Perovskite Lead Titanate at Reduced Temperatures: Possible Formation of Heterometallic (Pb,Ti)-Citric Acid Complex. *Chemistry of Materials*, Vol. 9, No. 2, 1997, pp. 451–456.

Appendix

Figure S1: UV-Visible absorption spectra of the perovskite powders.