

Fabrication of perovskite lanthanum orthoferrite as a photocatalyst for controlled atom transfer radical polymerization of methacrylate monomers toward an electrolyte material for lead acid batteries

Huong Thi Le^{1,2}, Tien Anh Nguyen², Thu Hoang Vo¹, Michal Michalak³,
Tam Hoang Luu⁴, Ha Tran Nguyen^{1,4*}

¹National Key Laboratory of Polymer and Composite Materials, University of Technology, Vietnam National University, Ho Chi Minh city, Vietnam

²Faculty of Chemistry, Ho Chi Minh city University of Education, Vietnam

³Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Poland

⁴Faculty of Materials Technology, University of Technology, Vietnam National University, Ho Chi Minh city, Vietnam

Received 10 January 2020; accepted 8 April 2020

Abstract:

Lanthanum orthoferrite (LaFeO₃) photocatalysts were synthesized by a facile and cost-effective coprecipitation method via the hydrolysis of La (III) and Fe (III). The characteristics of LaFeO₃ were investigated through thermogravimetric analysis (TGA), X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (DRS), vibrating sample magnetometry (VSM), and transmission electron microscopy (TEM). During the investigation of the applicability of LaFeO₃ as a photocatalyst for the atom transfer radical polymerization (ATRP) of methyl methacrylate monomer under UV irradiation, the obtained poly(methyl methacrylate) exhibited a high molecular weight and narrow polydispersity index. In addition, the LaFeO₃ can be recovered via application of a magnetic field and reused for the atom transfer radical polymerization process.

Keywords: ATRP, lanthanum orthoferrite (LaFeO₃), methacrylate, photocatalysts.

Classification number: 2.2

Introduction

One of the most important achievements made by humanity in the 20th century is the development and application of powerful synthetic polymeric materials. Polymeric materials have since been widely used in daily life due to their superior mechanical properties, low cost, and variety of applications such as in chemicals, electricity, electronics, and biomedicine.

A polymer's properties depend on their molecular weight, multiple dispersion, and molecular structure; all of which determine its various applications. Further, these factors are influenced by the method of synthesis. ATRP is a process that allows control of the molecular weight according to the polymer's original design and multi-level narrow dispersion. ATRP is a useful and widely used method within a larger system of polymer-free polymerization methods. Traditional ATRP is advantageous because the method is cheap and easy to implement via readily available catalysts on the market. However, its weakness is the existence of a residual metal that is hard to remove or exclude from the product [1]. This factor limits the application of the polymer product in fields requiring a high level of cleanliness, such as medicine and biomedicine [2].

Because of this disadvantage existing in traditional ATRP, a method called Organocatalyzed atom transfer radical polymerization (O-ATRP) was created, which uses organic catalyst alternatives in place of the metal complex

*Corresponding author: Email: nguyentrinha@hcmut.edu.vn

catalysts. The advantages of O-ATRP are the reliable control of the molecular weight and polymer dispersion variability, and the organic catalyst can be completely separated from the polymer product in a straightforward manner by centrifugation or precipitation in suitable solvent systems [3]. However, limitations of O-ATRP do exist, such as difficulty controlling high molecular weight products. So, the goal of this study is to find new photocatalysts that address the difficulty in controlling high molecular weight. In addition, such a well-controlled obtained polymer could be applied to electrolyte materials in rechargeable batteries.

In recent years, perovskite-type materials have been of great interest and importance because of their excellent potential as solid fuel [4], solid electrolytes, actuators, electromechanical devices, and transducers [5] due to their crystal structure, magnetism, electric conductivity, piezoelectric, electro-optic properties, and catalytic activity. However, studies about the photocatalytic performance of perovskites for the polymerization process have not yet been reported. The catalytic oxidation and surface electronic states of LaFeO_3 based on a typical ABO_3 -type perovskite structure has been previously studied [6]. The excellent gas sensitivity and catalytic activity of LaFeO_3 has also been well investigated due to its high stability, non-toxicity, and small band gap energy [7]. In previous studies, LaFeO_3 's band gap was found to be in the range of 2.12 - 2.67 eV [6]. With this small band gap, LaFeO_3 has been used as a photocatalyst for the decomposition of water [8] and as a photocatalyst for the photochemical decomposition of some organic dyes under visible light irradiation [9]. In addition, LaFeO_3 has a magnetic nature [10] that allows straightforward recovery of the catalysts after the reaction.

While LaFeO_3 is a potential photocatalyst, there appears to be no other research in the world, to the best of the authors' knowledge, about the use of LaFeO_3 as a photocatalyst for the polymerization of free radicals.

Materials and methods

Materials

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH, methyl methacrylate (MMA), Tetrahydrofuran (THF), and Phenyl 2-bromo-2-methylpropanoate ($\text{C}_{10}\text{H}_{11}\text{BrO}_2$) were used in this work.

Instrumentation

Thermal analysis of the sample was recorded on a DTG-60H (Japanese Shimadzu) at the Faculty of Chemistry, Ho Chi Minh city University of Education, in a dry air environment with a temperature rise of $10^\circ\text{C}/\text{min}$ and a maximum temperature of 1100°C .

X-ray diffraction was measured on a D8 ADVANCE (Germany) at the National Key Laboratory of Polymer and Composite Materials, University of Technology, Vietnam National University, Ho Chi Minh city, with $\text{Cu-K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$), $2\theta=10\text{-}80^\circ$, 0.03° measurement step, and dwell time every 1 s.

Microstructural and morphological images were taken by TEM on a JEOL-1400 (Japan) at the National Key Laboratory of Polymer and Composite Materials, University of Technology, Vietnam National University, Ho Chi Minh city.

The diffuse reflectance UV-Vis (DRS) of the material was determined by a JASCO 500 at the Institute of Applied Materials Science, which was fitted with a ISV-469 solid sample meter and using the BaSO_4 standard sample.

$^1\text{H-NMR}$ spectra were recorded in deuterated chloroform (CDCl_3) with tetramethylsilane as an internal reference on a Bruker Avance 500 MHz NMR spectrometer.

The spectra from gel permeation chromatography (GPC) were recorded at the National Key Laboratory of Polymer and Composite Materials, University of Technology, Vietnam National University, Ho Chi Minh city, on a polymer PL-GPC 50.

Synthesis of lanthanum orthoferrite (LaFeO_3)

LaFeO_3 nanomaterials were synthesized by slowly adding a small mixture of 1:1 $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into a cup of boiling water under constant magnetic stirring. After the salt mixture dissolved, boiling was continued for another 5-7 min, and then the mixture was allowed to cool. After slowly adding the NaOH solution to the mixture obtained above, excess NaOH was taken to collect the excess precipitates of the La^{3+} and Fe^{3+} cations (the filtered water was tested with a few drops of phenolphthalein). The precipitate was stirred on a stirrer for about 20 min, then filtered and washed several times with distilled water and dried naturally at room temperature for 3 d. After drying, the precipitate was finely ground and then heated under

air pressure from room temperature to several different temperatures to check the crystallization perfection and to create a homogenous phase of LaFeO_3 . The heating rate was $10^\circ\text{C}/\text{min}$.

General synthesis of polymers

Polymer methyl methacrylate (PMMA) was synthesized via UV light-induced ATRP using a Phenyl 2-bromo-2-methylpropanoate (PhBMP) initiator and LaFeO_3 as the photocatalyst. In a typical experiment, 10.01 mg ($41 \mu\text{mol}$) of PhBMP initiator was placed in a 25 ml flask, and 1 ml of degassed THF was added by a syringe. The solution was stirred until it became a homogeneous solution. Then, the MMA monomer (0.44 ml, 4.1 mmol) and LaFeO_3 (1 mg, $0.4 \mu\text{mol}$) were added separately. The mixture was degassed by three freeze-pump-thaw cycles. The solution was continuously stirred until it became homogeneous and placed in a UV-box (wavelength of 365 nm) for 24 h at room temperature. Finally, the resulted polymer solution was precipitated in cold methanol, followed by drying under vacuum, to give the desired product.

Results and discussion

Structure and properties of LaFeO_3

Figure 1 shows the DSC and TGA curves for the sample prepared by co-precipitation. A 19.16% weight loss of the

entire sample can be seen during the heating process from room temperature to 1000°C . Many reactions are observed from the DrTGA curve, occurring from about 40°C to 800°C . All of these processes can be distinguished into three phases.

Phase 1 occurs from 40°C to about 200°C . In this phase, a weight loss of 8.344% took place, which corresponds to an endothermic peak in the DSC curve at 98.59°C caused by surface desorption and dehydration [11]. The second phase of mass reduction occurred between 400°C and 500°C with a mass loss of 7.783%, which corresponds to an endothermic peak at 462.19°C due to nitrate-based pyrolysis [12]. The third mass reduction phase, from 500°C to 800°C , includes the pyrolysis hydroxides of $\text{La}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, and base-carbonate salt pyrolysis of $\text{La}_2(\text{CO}_3)_{3-x}(\text{OH})_{2x}$. The occurrence of base-carbonate salts in the precipitation after drying of rare earth element ions, especially La^{3+} , has been published in the research of Nagashima Kozo's group [13]. At 800°C and upwards, the TG path is almost horizontal. From the thermal analysis scheme, the sample heating temperature is 900°C . Investigation of single-phase LaFeO_3 formation was analysed by X-ray diffraction. The results are shown in Fig. 2. The XRD diagram of LaFeO_3 was taken at 900°C . The diagram shows only single-crystal phase peaks of the LaFeO_3 perovskite and no impurities peaks were

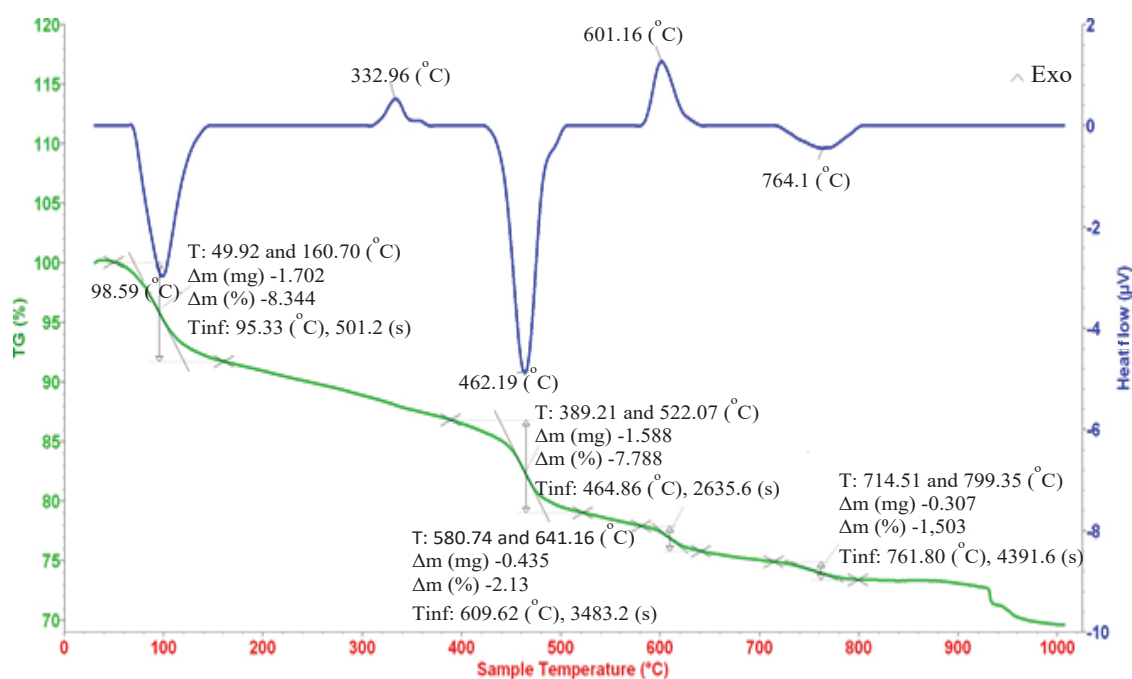


Fig. 1. Thermal analysis diagram of LaFeO_3 .

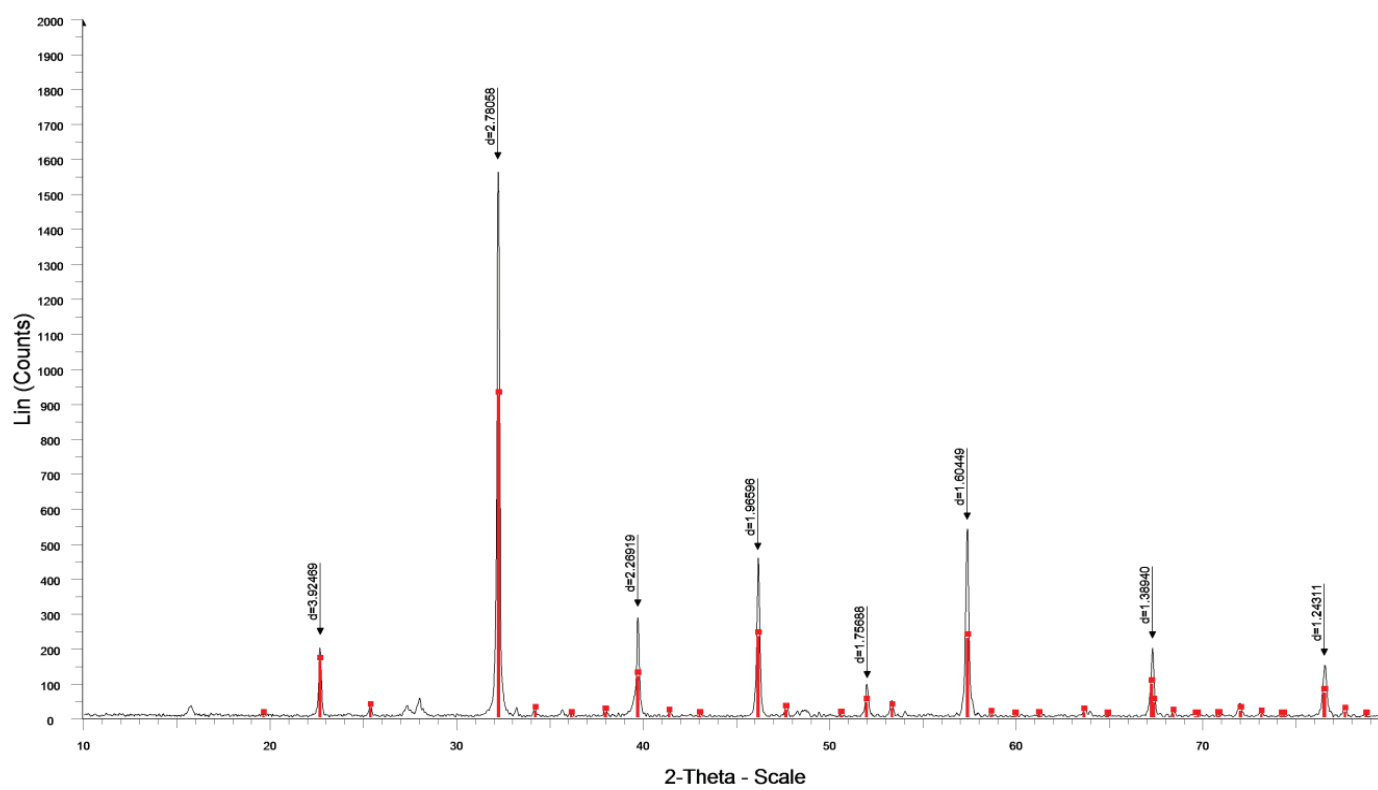
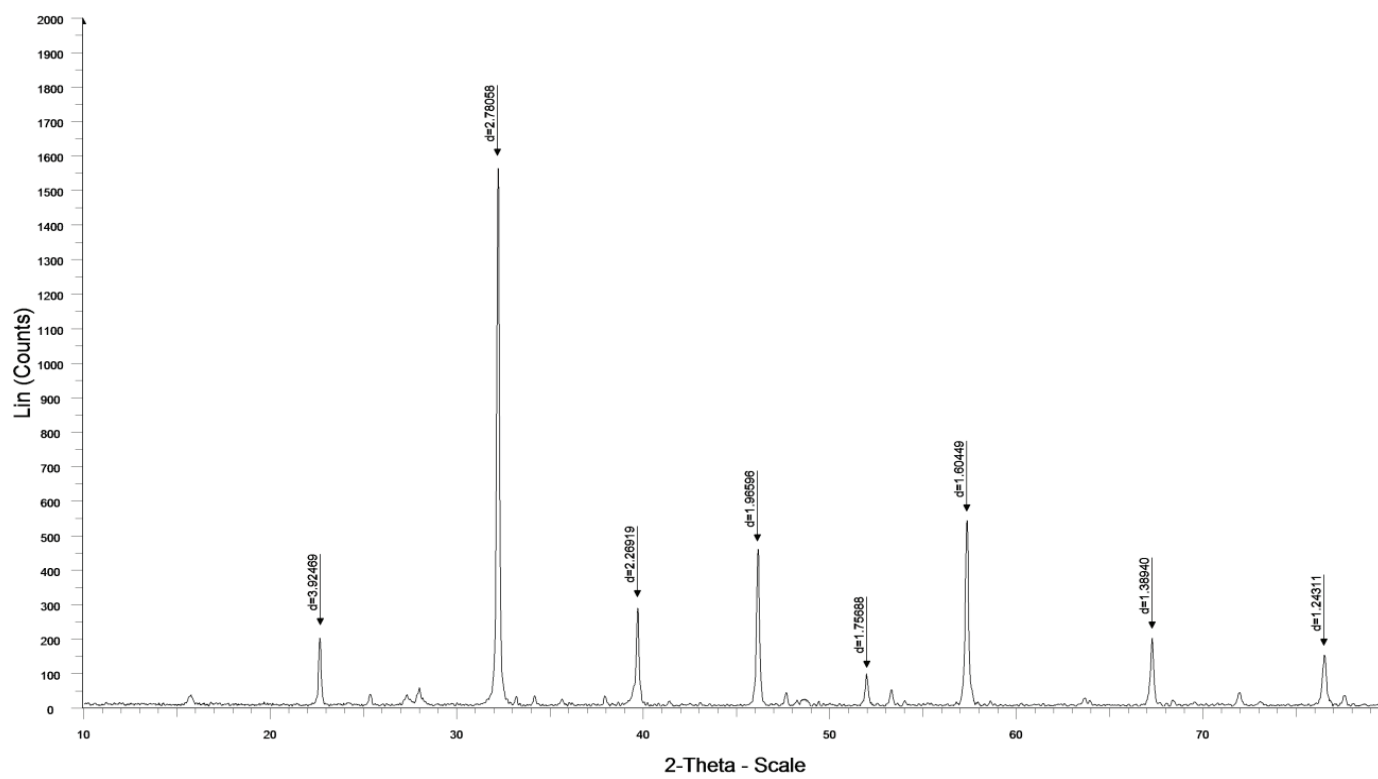


Fig. 2. (A) XRD spectra of LaFeO_3 obtained at 900°C ; (B) XRD spectrum of LaFeO_3 obtained overlapped with the standard spectrum.

observed. The TEM results of the sample baked at 900°C showed LaFeO₃ nanoparticles have a spherical shape and are 50-70 nm in size (see Fig. 3).

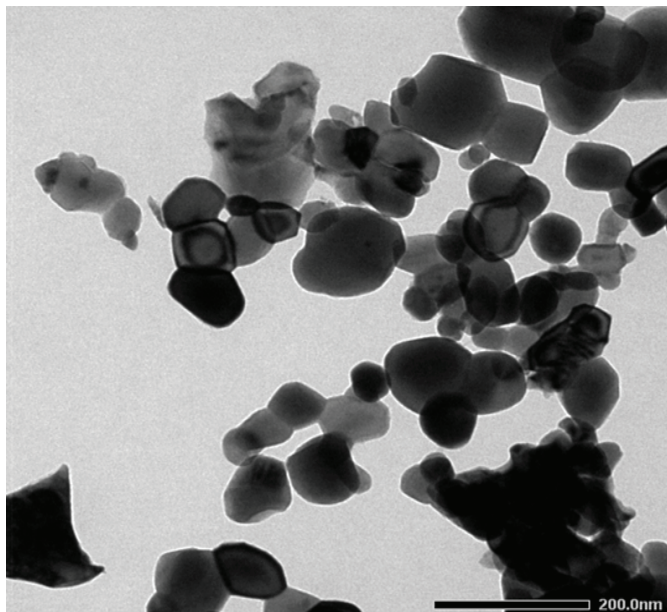


Fig. 3. TEM image of LaFeO₃ prepared by the co-precipitation method, followed by calcination at 900°C.

Figure 4 shows the magnetization curves of LaFeO₃ nanopowders measured at room temperature by VSM. The magnetic characteristics of LaFeO₃ nanomaterials samples at room temperature after calcination at 900°C show that the magnetic resistance (coercive field) value H_c=35.375 Oe, proving that the synthesized LaFeO₃ material is a soft magnetic material.

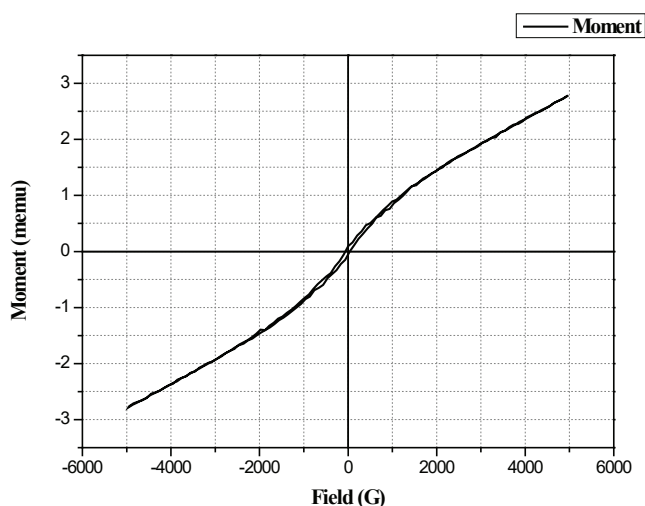


Fig. 4. The room temperature hysteresis loop of LaFeO₃ after calcination at 900°C.

The UV-Vis spectrum of the LaFeO₃ nanopowder is shown in Fig. 5. The UV-Vis results show that the catalyst can absorb spectral energy over a wide range between 350-800 nm and that LaFeO₃ absorbs maximum light at 411 nm with 93.63% absorption. These results prove that LaFeO₃ is a potential catalyst in the photocatalytic field.

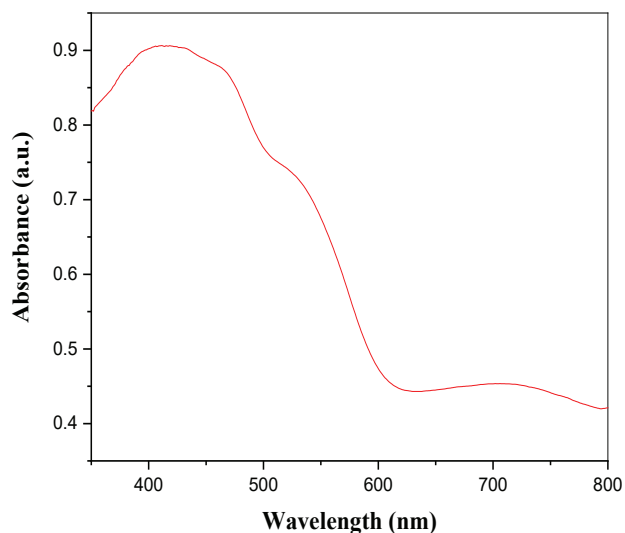


Fig. 5. DR UV-Vis spectra of 900°C-activated LaFeO₃.

A regression equation was established using the UV-Vis results of the ferrite perovskite LaFeO₃, with $y=5.8361x-10.56$ and a correlation coefficient $R^2=0.9501$. Based on the onset optical absorption (Fig. 6), the band gap of the LaFeO₃ material can be estimated to be about 1.809 eV.

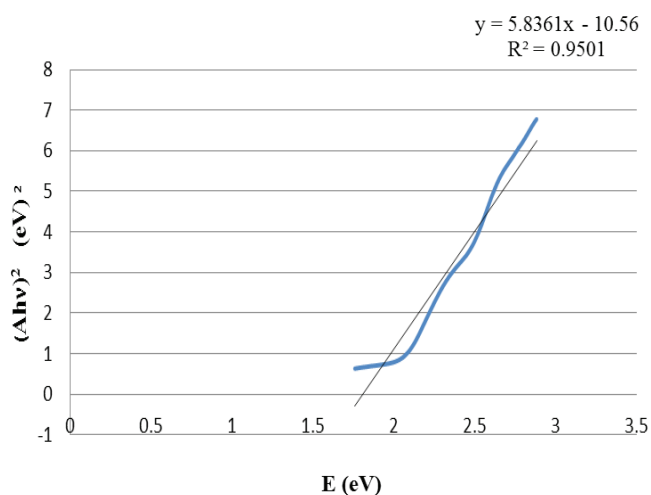


Fig. 6. The regression equation from UV-Vis of the ferrite perovskite LaFeO₃.

Investigation of the possibility of polymerization of methyl methacrylate

According to photocatalysts used in ATRP-based research from Hawker, Matyjaszewski, and Miyake, we used LaFeO_3 as the photocatalyst for ATRP of the MMA monomer. The ATRP of the MMA monomer involves photoexcitation of the LaFeO_3 catalyst to an excited state of LaFeO_3 under UV irradiation. The proposed mechanism of polymerization is illustrated in Fig. 7.

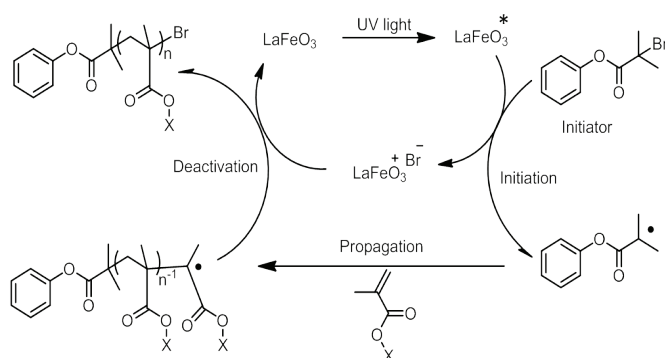


Fig. 7. Proposed mechanism for ATRP using LaFeO_3 .

The obtained PMMA was characterized via $^1\text{H-NMR}$, as seen in Fig. 8, to determine its structure. The polymerization of MMA using the photocatalyst LaFeO_3 was carried out with the ratio $[\text{Monomer}]:[\text{Initiator}]:[\text{LaFeO}_3]=100:1:0.1$. The obtained polymer was precipitated in cold methanol and characterized by GPC to determine the average molecular weight. It should be noted that the molecular weight of the formed polymer is approximately equal to the designed molecular weight. The results of MMA polymerization using the LaFeO_3 catalyst are presented in Table 1.

Table 1. Macromolecular characteristics of PMMA synthesized by ATRP using the LaFeO_3 catalyst.

$[\text{MMA}]:[\text{I}]:[\text{LaFeO}_3]$	M_n (g/mol)	M_w (g/mol)	Dispersity (PDI)
$[100]:[1]:[0.1]$	35740	38200	1.09

Conclusions

LaFeO_3 nanomaterials were synthesized by coprecipitation through the slow hydrolysis of La^{3+} and Fe^{3+} cations in boiling water with NaOH as the precipitating agent. LaFeO_3 nanomaterials formed after calcination and

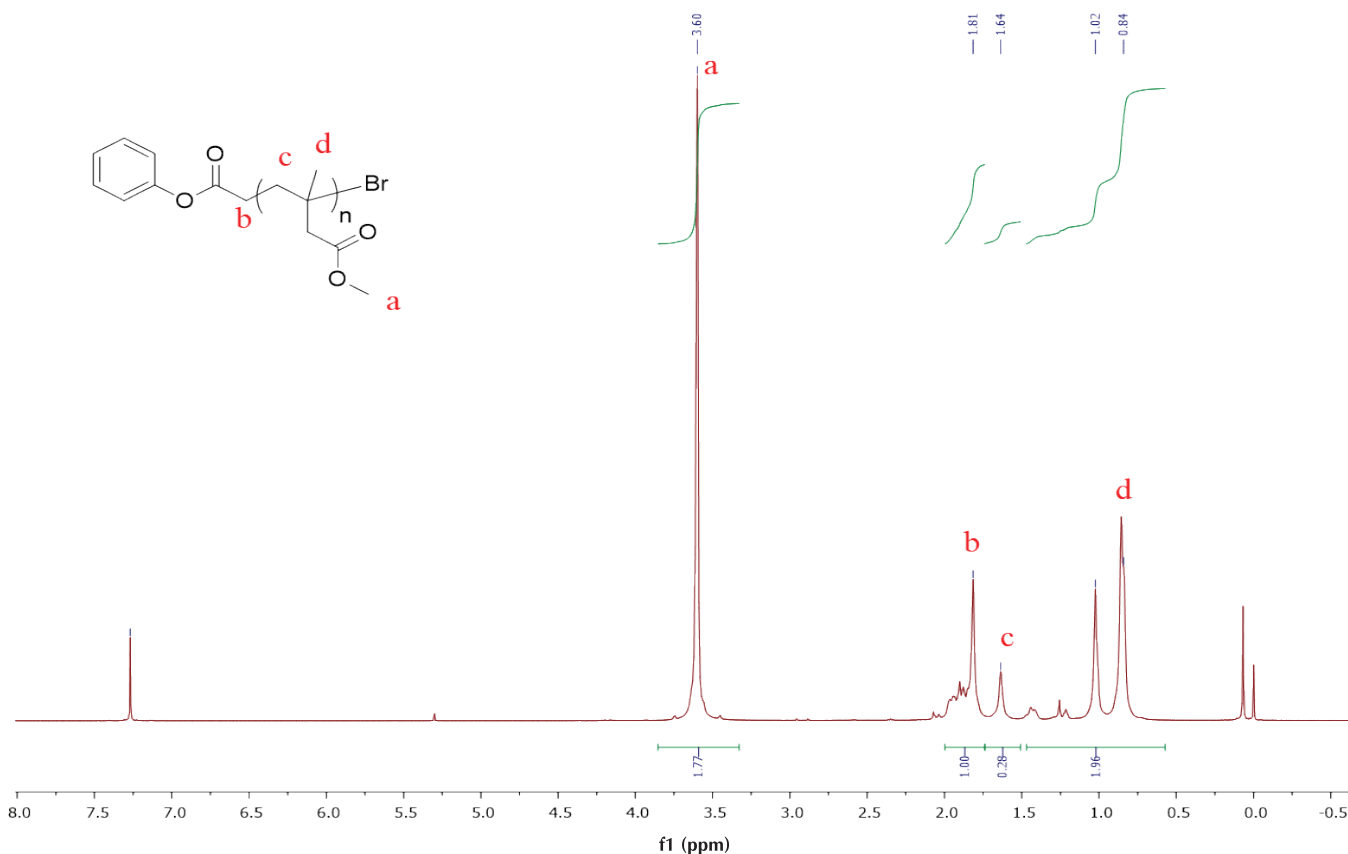


Fig. 8. $^1\text{H-NMR}$ spectra of PMMA.

precipitation at 900°C with particle sizes of 50-70 nm. LaFeO₃ proved to be an efficient catalyst for ATRP, which produced polymethacrylates with a controlled molecular weight of 38200 g/mol, as well as a narrow polydispersity of 1.09 by UV irradiation. The obtained PMMA exhibited a high molecular weight and narrow polydispersity index. In addition, the LaFeO₃ was recovered via magnet field application and reused for the atom transfer radical polymerization process. Furthermore, the well-controlled PMMA could be investigated as a solid electrolyte material for rechargeable batteries in a prospective research study.

ACKNOWLEDGEMENTS

This research is funded by University of Technology, Vietnam National University, Ho Chi Minh city, under grant number T-CNVL-2019-24.

The authors declare that there is no conflict of interest regarding the publication of this article.

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