



# Microwave-assisted synthesis of nanostructured perovskite-type oxide with efficient photocatalytic activity against organic reactants in gaseous and aqueous phases

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## ABSTRACT

Microwave-assisted synthesis as a straightforward, efficient and time-saving approach is used for the synthesis of LaFeO<sub>3</sub> nanoparticles. The obtained perovskite showed a narrow band gap energy (2.12 eV), high crystallinity, great oxygen adsorption/ desorption ability and mesoporous structure. In order to assess the photocatalytic activity, benzene and reactive black 5 (RB5) dye are used as gaseous and aqueous reactants, respectively. Under visible light irradiation, almost 85% benzene and 96% RB5 degradation are obtained over the perovskite. The reactions are monitored for 60 min using Gas Chromatography (FID & TCD) and UV-VIS spectrophotometer. The dye degradation process is studied thoroughly, from the mechanistic point of view. Surface charge density of LaFeO<sub>3</sub> is measured at different dye concentration to identify the electrical nature of the surface whether it is positive or negative. Moreover, a series of reactions are conducted to monitor the effect of scavengers on the rate of the photocatalytic dye degradation and decipher which active species (hydroxyl and superoxide radicals or the holes) have dominated the dye oxidation reaction. In the present study, hydroxyl radicals are found as the main active species in the photocatalytic degradation reaction.

## 1. Introduction

Nowadays, semiconductors, especially metal oxides are the most promising materials with photocatalytic properties for clean solar energy production along with an assuring environmental treatment for water and air purification [1–3].

Among the vast variety of the semiconductors, TiO<sub>2</sub> immensely attracted public attention due to its remarkable activity and stability under irradiation as well as low-cost and eco-friendliness [4,5]. Notwithstanding the considerable features, TiO<sub>2</sub> faces with many limitations in empirical applications due to its high bandgap energy (3.0 eV)—it merely exhibits activity under UV light illumination that accounts for < 4% of solar energy [6]. Even though there have been many efforts made to modify the photo-responsive activity of TiO<sub>2</sub> (with the intention of diminishing the bandgap energy to make it active in the visible region) [7–9], the obtained materials encountered serious problems such as instability, nonviability, and low-efficiency. With respect to these issues, prior to any movement, introducing the

innovative experimentations and development of feasible and applicable visible light responsive materials could be vital in the field of photocatalysis. In this case, perovskite type oxide materials are in the centre of attention as a result of their unique intrinsic properties, especially their tremendous oxygen mobility [10,11]. Among the wide range of perovskites, LaMO<sub>3</sub> has intensively attracted as a cost-effective, earth-abundant and efficient photocatalyst that has the merit of being visible light responsive. This structure benefited by the possibility to replace the “M”, which makes it an appropriate candidate for structural engineering with the purpose of declining the bandgap energy. In other words, differing the M (with different size of metals) not only leads to dominating the bandgap energy but also culminated in the controlling of the surface's energetic alignments such as oxygen vacancies (results in the enhanced photocatalytic activity) [12,13]. In this context, LaFeO<sub>3</sub> (bandgap, ~2.36 eV) is one of the most prospective perovskites, which is used as fuel cells, solid electrolytes, gas sensors and superconductors as well as a pollution remedy agent [14–16]. For decades, these materials have been prepared by various

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methods such as sol-gel, hydrothermal and co-precipitation as well as solid state synthesis. However, these approaches have some intrinsic drawbacks from chemistry and environmentally points of view, such as sophisticated catalyst preparation, calcination course (high temperature is inevitable) and time-consuming process, as well as reliance on pH adjustment [17,18]. While the microwave-assisted method emerged as a new manner of synthesis and considerably investigated in the terms of organic and/or inorganic synthesis due to the number of distinct benefits such as time-saving (quick reaction), homogeneous microwaving, along with the green and efficient energy applications [19,20]. Therefore, these features make it an appropriate candidate for the preparation of  $\text{LaFeO}_3$ .

Preserving the environment is a global concern for sustainable development [21]. In terms of the environment, the catastrophic effect of increasing air and water pollution on the ecosystem has been alarming for living organisms. In the same context, benzene as an air pollutant is one of the eight representative indoor volatile organic compounds (VOCs) [22,23], which has a solely stable structure due to its high oxidation potential. This durability makes it an excellent choice as an organic reactant to evaluate the photocatalytic activity [24–26]. For a past few decades, with the development of textile industries, eliminating of the organic pollutants, such as reactive dyes, with markedly stable azo groups ( $\text{N}=\text{N}$ ), has turned to a primary problem. However, these contaminants have removed by non-catalytic approaches that are toxic and expensive [27]. Therefore, there is an urgent requirement for the environmentally benign routes to overcome the obstacles such as photocatalytic eradication of the pollutants.

In this report, to overcome the above issues, mesoporous  $\text{LaFeO}_3$  nanoparticles with a narrow bandgap energy were synthesised using microwave-assisted approach. Then, they were characterised thoroughly to evaluate the perovskite structure from physical and chemical points of view. Afterwards, the photocatalytic activity was examined under visible light irradiation to check whether it takes an active role in the oxidation of RB5 and benzene or not. Finally, a series of experiments such as measuring the surface charge density and the scavenger study [28,29] were performed with a mechanistic approach to identify the active species in the photocatalytic oxidation of the dye.

## 2. Material and methods

### 2.1. Preparation of $\text{LaFeO}_3$ powders

All precursors were purchased from Sigma-Aldrich. The microwave-assisted approach is used to synthesise  $\text{LaFeO}_3$  nanoparticles. In this context, appropriate amounts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.1 M, 99.0%) and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 M, 99.0%) were dissolved in deionized water at room temperature under constant magnetic stirring for almost 1 h. Afterwards, the solution transformed to a microwave appliance and kept under microwave exposure (850 W) until obtaining of a red-brick powder [19]. The powder was washed thoroughly with deionized water to remove any excess residue. Then, it is transferred to an oven and kept for 2 h at 80 °C, the obtained powder is used as a photocatalyst in the further reactions.

$\text{LaFeO}_3$  nanoparticles were characterised by XRD with a scanning rate of  $0.02 \text{ s}^{-1}$  in a  $2\theta$  range from  $0^\circ$  to  $70^\circ$  (Rigaku Ultima instrument with Cu K radiation  $1.5408 \text{ \AA}$ ) and the data were analysed by JCPDS standards. The specific surface area and maximum pore size distribution were obtained from the BET and BJH equations (Micromeritics). Furthermore, the UV-visible diffuse reflectance spectra (DRS) was scanned in the range of 200 and 700 nm using a Varina-Carry 100 double beam UV-Vis spectrophotometer. The  $\text{H}_2$ -TPR (Micromeritics Chemisorb 2750 apparatus, 5 vol%  $\text{H}_2/\text{Ar}$ ) was used to analyse the oxygen reducibility of the catalyst. Furthermore, a high resolution field emission HR-TEM (FEI Tecnai G2, Japan) provided the analysis with the accelerating voltage up to 300 kV. Surface morphology analysis is also performed by SEM (JSM-7600F; JEOL, USA).

### 2.2. Photocatalytic reaction

#### 2.2.1. Photocatalytic benzene oxidation

Photocatalytic oxidation of gaseous benzene over the photocatalyst under visible-light irradiation was carried out in a glass photoreaction cell with an effective volume of 80 mL that has been attached to a homemade glass manifold with a volume of 174 mL (Fig. S1). The manifold was wrapped by a heating tape to keep the temperature at 95 °C. A vacuum pump was connected to the manifold for evacuation of benzene after every run of the photocatalytic oxidation reaction. An adequate amount of photocatalyst, which has already been coated on the beads, was placed in the photoreaction cell. Then, the whole manifold was under vacuum for 30 min to remove any gas from the photoreaction cell. Next, 2  $\mu\text{L}$  of liquid benzene was injected to manifold from injection chamber, benzene was allowed to evaporate in the manifold for 20 min, and the air was introduced to the system by opening the air valve. Afterwards, photoreaction cell's valve is left open for 10 min to let flow the benzene and air into it, after the completion of adsorption-desorption of gases on the surface of the photocatalyst, it was illuminated by visible light source (60 W tungsten lamp) for 60 min. Finally, the reaction process has been monitored by injections from photoreaction cell every 10 min consecutively. In the same context, the concentration of benzene and  $\text{CO}_2$  simultaneously were evaluated using GC-TCD-FID (HP 6890 GC with TCD-FID).

#### 2.2.2. Photocatalytic dye decolourization

The commercial colour index (CI) dye (Reactive black 5, molecular weight = 991.82 g) was used without further purification (Fig. S2). The pH value was adjusted by an Elmerton CP-501 pH-meter. The initial pH of the sample was tuned by using dilute sodium hydroxide (0.5 M) or hydrochloric acid (0.5 M). The initial concentration of the dye and amounts of  $\text{LaFeO}_3$  nanoparticles were 100 ppm and 100 mg, respectively. The dye removal experiments conducted at 25 °C and the pH range were from 1 to 10. The photocatalyst is separated from the dye solution by centrifuging, then the obtained solution was analysed. The concentration of the dye in the reaction mixture was monitored at the different reaction time (Shimadzu, UV-2550, Japan) by measuring the absorption intensity at  $\lambda_{\text{max}} = 596 \text{ nm}$  with a calibration curve. All experiments conducted three times to be assured about the data replication, then the average of the measurements was reported. It is noteworthy to mention that all the experiments were operated at room temperature under visible light.

#### 2.2.3. Measurements of surface charge density

Generally, the surface charge of metal oxides is determined by potentiometric titration. Fundamentally, comparison of the water's titration curve obtained at various pH values (from 3 to 10) with the titration curve of dye solution (50 and 100 ppm of dye concentration in the same range of pH) leads to  $\text{pH}_{\text{zpc}}$  (pzc: point of zero charges) determination. In addition, the volume difference ( $\Delta V$ ) obtained from the titration of water and dye solution with an alkali solution (NaOH solution, 0.1 mol/L) in order to adjustment of pH, results in the measurement of the surface charge density (Eq. (1)).

$$\sigma_0 = \frac{\Delta V \cdot C_b \cdot F}{m \cdot S} \quad (1)$$

where  $C_b$  (mol/L) is alkali solution's concentration,  $F$  (C/mol) is the Faraday constant, as well as  $S$  ( $\text{m}^2/\text{g}$ ) and  $m$  (g), which are the surface area and quantity of the perovskite, respectively. The measurements were performed with the composition of the following instruments: Teflon vessel, cooling thermostat (RE204-Lauda), burette Dosimat 665 (Metrohm), pH meter (Elmerton CP-501) which were connected to a computer. In this context,  $\text{LaFeO}_3$  nanoparticles ( $m = 100 \text{ mg}$ ) was added into the container (room temperature) along with dye solution/pure water up to 50 mL. Then the surface charge density was obtained from the water's titration curve.

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