

ORIGINAL ARTICLE

Photocatalytic plate-like $\text{La}_2\text{Ti}_2\text{O}_7$ nanoparticles synthesized via liquid-feed flame spray pyrolysis (LF-FSP) of metallo-organic precursors

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Abstract

Nanoparticles (NPs) of a perovskite-slab-type oxide, $\text{La}_2\text{Ti}_2\text{O}_7$, were synthesized using LF-FSP coupled with subsequent heat treatments, and their photocatalytic activity was evaluated using decolorization of methyl orange solution under Uv irradiation. The LF-FSP process used metallo-organic precursors to produce NPs with very low agglomeration with average particle sizes (APSs) of 26 nm (LF-FSP NP). Optimized heat treatment of these NPs at 1000°C/3 h/air gave small, plate-like NPs with high crystallinity, and BET specific surface areas (SSAs) of 14 m²/g, that exhibited the best observed photocatalytic activity. High-angle annular dark-field scanning TEM showed that heat-treating eliminates microstructural defects in these NPs, improving photocatalytic activity by ≈30%. The current approach to perovskite-slab-type NPs using LF-FSP provides a simple route to materials with superior photocatalytic activity and offers the advantage of good productivity, 30 g/h.

KEYWORDS

$\text{La}_2\text{Ti}_2\text{O}_7$, liquid-feed flame spray pyrolysis, nanoparticle, perovskite-slab-type compound, photocatalyst

1 | INTRODUCTION

Liquid-feed flame spray pyrolysis (LF-FSP) is a unique approach to obtaining ceramic nanopowders (NPs) via aerosolization of alcohol solutions containing controlled concentrations of mixtures of metallo-organic compounds into a flame in flowing oxygen carrier gas that is ignited using methane/oxygen torches generating a cloud of ions at ≈1200°C. This cloud is quickly quenched to produce unaggregated NPs typically with the same composition as in the original solution^{1,2} without using hot surfaces as the heat source.³ LF-FSP processed NPs typically offer APSs of 25–70 nm and narrow size distributions not easily obtained using precipitation methods with conventional metal salts such as nitrates and chlorides.⁴ LF-FSP gives ≈30 g/h NPs. Moreover, owing to rapid quenching, the largely unaggregated NPs are readily dispersible providing access to a wide variety of thin, dense, flexible, and functional, thin ceramic films, 5–60 μm.^{5–8}

The work reported here concerns the LF-FSP synthesis of perovskite-related layered compounds that have attracted considerable attention because of their multiple interesting properties, such as high temperature superconductivity,^{9,10} ferroelectricity,^{11,12} ferromagnetism,^{13,14} and photocatalytic activity.^{15,16} They can be classified into three main groups^{17,18}; Ruddlesden-Popper- $(\text{A}_{m+1}\text{B}_m\text{O}_{3m+1})$, Aurivilleus- $(\text{A}_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3})$, and perovskite-slab-type $(\text{A}_m\text{B}_m\text{O}_{3m+2})$. In all types, A is a large 12 co-ordinate cation, B is a small 6 co-ordinate cation, and the layers are m BO_6 octahedra thick.

$\text{La}_2\text{Ti}_2\text{O}_7$, the focus here, belongs to the perovskite-slab group. $\text{La}_2\text{Ti}_2\text{O}_7$ is a well-known ferroelectrics having a Curie temperature of 1773 K.^{19–21} Several different values for its band gap (3.29–4.05 eV) have been reported.^{22–25} Kim et al²⁶ first reported that $\text{La}_2\text{Ti}_2\text{O}_7$ could be used to photocatalytically split water under UV light. Periodically arranged corner-shared TiO_6 octahedra boost charge mobility providing quantum yields as high as 27% especially for Uv-promoted photocatalytic water splitting.^{24,27}

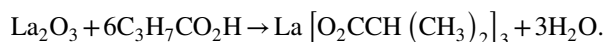
Several approaches to properties improvement have been studied including solid-state reactions,²⁸ polymerizable complex methods,^{27,29,30} spray pyrolysis,³¹ metallo-organic decomposition,³² hydrothermal,³³⁻³⁵ and flux synthesis methods.³⁶⁻³⁸ Furthermore, N-doping has been explored targeting visible-light photocatalytic behavior.^{38,39}

In this study, we first synthesized the perovskite-slab-type $\text{La}_2\text{Ti}_2\text{O}_7$ NPs using LF-FSP from simple metallo-organic precursors coupled with a post heat treatment providing access to suitable materials whose photocatalytic activity for degradation of methyl orange solutions was subsequently examined. In particular, we were able to process $\text{La}_2\text{Ti}_2\text{O}_7$ NPs with high crystallinity and large surface areas from the flame-made NPs and compared their characteristics with materials prepared by other methods reported previously.

2 | EXPERIMENTAL

2.1 | NPs syntheses through LF-FSP

NPs were prepared via LF-FSP using the metallo-organic precursors; lanthanum isobutyrate $\{\text{La}[\text{O}_2\text{CCH}(\text{CH}_3)_2]_3\}$ and triethanolamine titanate ($\text{C}_6\text{H}_{17}\text{NO}_6\text{Ti}$). Triethanolamine titanate was purchased (MP Biomedicals, LLC, technical grade). Lanthanum isobutyrate was synthesized by reaction of lanthanum oxide with isobutyric acid. The detailed conditions are described in our previous paper.⁵



The ceramic yields of each precursor were measured by TGA.⁵ The precursors were dissolved in ethanol at stoichiometric molar ratios (La:Ti = 1:1) to give a 3 wt. % ceramic yield solution. The precursor solution was aerosolized with oxygen with flow speed of 50 mL/min into a stainless steel chamber where it was combusted with methane/oxygen pilot torches in an oxygen-rich environment. Combustion of solvent and organic ligands creates a plume of ions that are quenched and quickly condense to unaggregated NPs, which were collected in downstream by rod-in-tube electrostatic precipitators operated at 10 kV. Figure 1 presents a schematic of the apparatus. The LF-FSP process was detailed in a previous paper.¹

The LF-FSP NPs were then heat-treated at 900-1200°C/0-6 h/air using an electric furnace (MTI Corporation, GSL1600X) to optimize photocatalytic properties.

2.2 | Characterization

Powder X-ray diffraction (XRDs) analyses were run on a Rigaku Rotating Anode Goniometer for simple phase

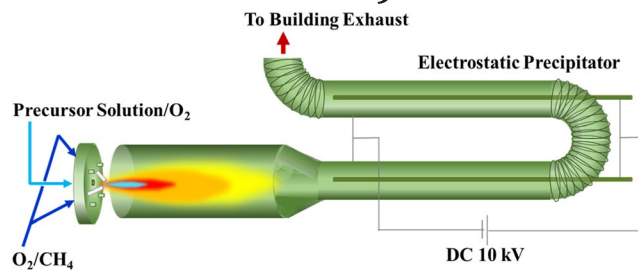


FIGURE 1 Schematic diagram of apparatus of liquid-feed flame spray pyrolysis [Color figure can be viewed at wileyonlinelibrary.com]

determination of the NPs. Scans were from 10 to 70° 2 θ , using graphite-monochromator-filtered $\text{CuK}\alpha$ radiation operating at 40 kV and 100 mA.

Fourier transform infrared (FTIR) spectra were recorded using Nicolet 6700 Series FTIR spectrometer (Thermo Fisher Scientific, Inc) in KBr dispersions in the range of 400-4000 cm^{-1} .

Brunauer-Emmett-Teller (BET) surface areas were determined using ASAP 2020 sorption analyzer (Micromeritics Inst.) from nitrogen adsorption isotherms and using AS1-MP and AS-iQ sorption analyzer (Quantachrome Inst.) from krypton adsorption isotherms.

Scanning electron microscopy (SEM) was run on a JEOL JSM-IT500 to observe the NPs.

All samples were sputter coated with Au/Pd using an SPI sputter coater. Average particle sizes (APSs) of LF-FSP NPs were determined from size measurement of more than 100 particles in the SEM images.

Transmission electron microscope (TEM) and a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were run at 200 kV on JEOL JEM-ARM200F for observation of microstructure of the NPs. Selected area electron diffraction (SAED) was also run to estimate crystallinity.

X-ray photoelectron spectroscopy (XPS) analysis was run on ULVAC-PHI Versa Probe II for investigation of surface defects of the NPs.

UV-vis diffused reflectance spectra analysis was run on a Hitachi UH4150 spectrophotometer equipped with an integrating sphere to estimate a bandgap energy of the NPs.

2.3 | Photocatalytic evaluation

Photocatalytic activity was evaluated quantitatively by decolorization of methyl orange (MO) solutions with NP dispersions under UV irradiation. 15 mg of NPs was put into 15 g of 0.001 w/v % methyl orange solution, followed by ultrasonic dispersion for 5 min to obtain a suspension. Afterward, the suspension was placed in a dark place for 1 hour to adjust the powder surface to the solution. Then, it was irradiated

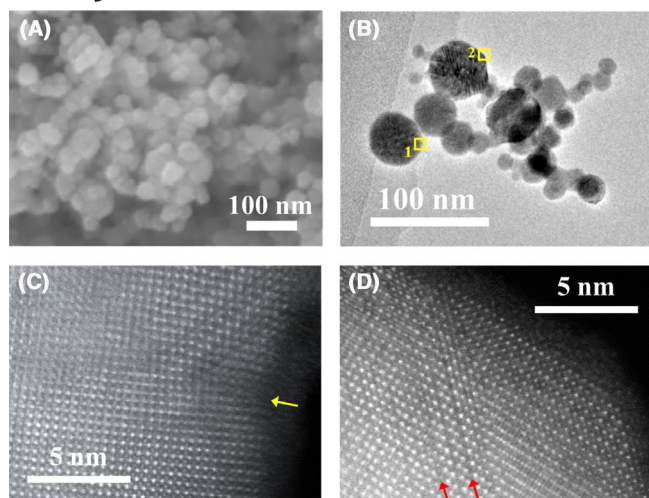


FIGURE 2 (A) SEM image and (B) STEM image of LF-FSP NP. HAADF-STEM images of (C) area 1 and (D) area 2 in image (B) [Color figure can be viewed at wileyonlinelibrary.com]

under UV by using a light source of 400W metal halide lamp for 0-60 minutes. The distance between the light source and the sample was 230 mm, and the suspension was not stirred but cooled during the irradiation. The suspended state could be kept up after the irradiation owing to the small size of the NPs.

The suspension was then transferred to a vial and centrifuged for 30 min. Then, the wavelength-dependent absorbance of the supernatant was measured using a UV-vis spectrophotometer (Agilent Cary 60). Absorbance of the MO solution at 464 nm was measured and calibrated by a plot of the absorbance at 464 nm as a function of the MO solution to obtain the MO concentration (C). Decolorization degree was estimated from calculating $((C_0 - C)/C_0) \times 100$ (%), where C_0 is initial MO concentration (0.001 w/v (%)). We confirmed almost no decolorization obtains without any photocatalyst, as a reference.

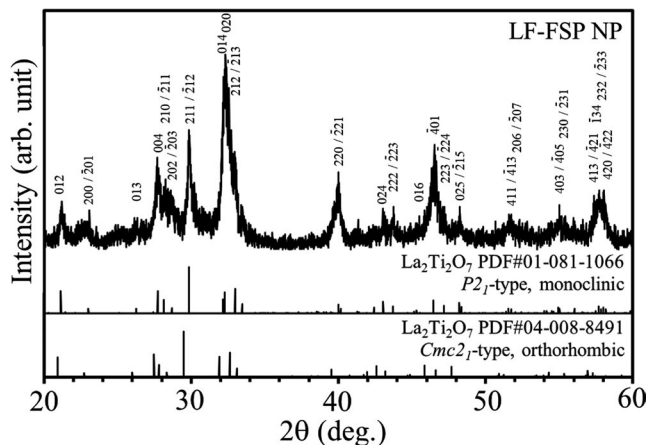


FIGURE 3 XRD pattern of LF-FSP NPs. Lattice planes corresponds to monoclinic $P2_1$ -type $\text{La}_2\text{Ti}_2\text{O}_7$

3 | RESULTS AND DISCUSSION

3.1 | LF-FSP NPs

Figure 2A provides SEMs of as synthesized NPs, consisting of small primary particles with APSs of ≈ 26 nm, low agglomerate contents, and no apparent necking. Note that the small primary particles do not form agglomerated large (>1 μm) secondary particles, as often observed in conventional spray pyrolysis products.^{3,40} The BET surface area was measured as 27 m^2/g .

A TEM image of the NPs is provided in Figure 2B, showing spherical faceted particles. Figure 2C,D provide HAADF-STEM images of areas 1 and 2 in Figure 2B, respectively. It can be seen that the NPs exhibit twin deformation (yellow arrow in Figure 2C) and irregular lattice disorder (red arrows in Figure 2D). Such microstructural defects are likely ascribed to NP formation through quenching from a cloud of gaseous ions at high temperatures in very short times.

Figure 3 XRD pattern exhibits diffraction peaks identified as $\text{La}_2\text{Ti}_2\text{O}_7$ (PDF#01-081-1066: $P2_1$ -type, monoclinic). Fluctuations in the lattice spacing due to the microstructural defects (Figure 2C,D.) and the low crystallinity broaden the diffraction peaks. Some multiple neighboring peaks seem to be connected to show single strong peaks. Ishizawa et al⁴¹ reported that the high temperature phase of $\text{La}_2\text{Ti}_2\text{O}_7$ (PDF#04-008-8491: $Cmc2_1$ -type, orthorhombic) is formed above approximately 780°C . This phase was not evident in our samples even though the NPs were formed by quenching from high temperature.

3.2 | Heat treatment of NPs

It is known that high crystallinity (low defect densities), high dispersion, and large surface areas favor superior photocatalytic activity.⁴² Thus, we explore heat-treating the NPs. To suppress the significant decrease in high dispersion and large SSAs, we explored heating at modest temperatures. Figure 4 provides XRDs for NPs heat-treated at 900 - $1000^\circ\text{C}/0$ h/air at $10^\circ\text{C}/\text{min}$. Although diffraction peak shapes remain unchanged at heat treatments below 950°C , they began to change at 1000°C , implying that diffusion leading to crystal growth commences. Therefore, we heat-treated the NPs at 1000°C at 0.5, 1.5, 3.0, 4.5, and 6.0 hours. All diffraction peaks could be clearly indexed to monoclinic $\text{La}_2\text{Ti}_2\text{O}_7$ with $P2_1$ -type space group (PDF#01-081-1066) for all heat-treated samples. A typical XRD for NPs heat-treated at $1000^\circ\text{C}/3$ h/air is shown in Figure 5.

The FT-IR spectrum of NPs heat-treated at $1000^\circ\text{C}/3$ h/air in KBr is provided in Figure 6. The spectra show two strong, broad absorption bands around 561 and 653 cm^{-1} , attributed

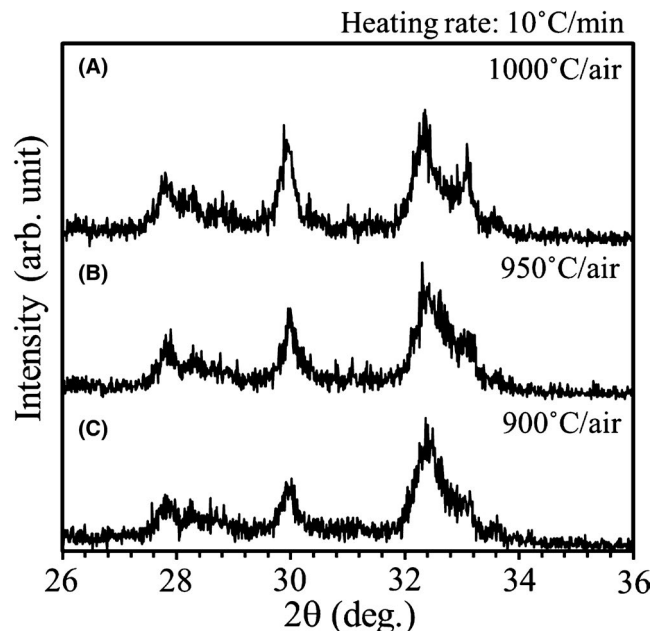


FIGURE 4 XRD patterns of heat-treated LF-FSP NPs. Heat-treat conditions; (A) 1000°C/0 h/air, (B) 950°C/0 h/air, (C) 900°C/0 h/air. Temperature raising speed: 10°C/min

to ν Ti-O in TiO₆ octahedra and ν La-O, respectively.^{43,44} Absorption bands around 466 cm⁻¹ are also found for ν La-O. Furthermore, small bands around 766 and 808 cm⁻¹ can be due to one short ν Ti-O bond in TiO₅ and TiO₄ units, respectively.⁴⁵

Figure 7A-C provide SEM images of NPs heat-treated at 1000°C/1.5 h/air, 1000°C/3 h/air, and 1000°C/6 h/air, showing that the size is increased with increase in the heat treatment time. The NPs heat-treated at 1000°C/3 h/air (Figure 7B) have plate-like morphologies approximately 100 nm in diameter and 20-30 nm thick. Weak aggregation seems to be maintained even after heat treatment. Figure 7D shows a STEM image of the NPs heat-treated at 1000°C/3 h/air, showing that the plate-like NPs are necked at the edges of each NP. HAADF-STEM image of area 1 in Figure 7D and SAED of area 2 in Figure 7D are

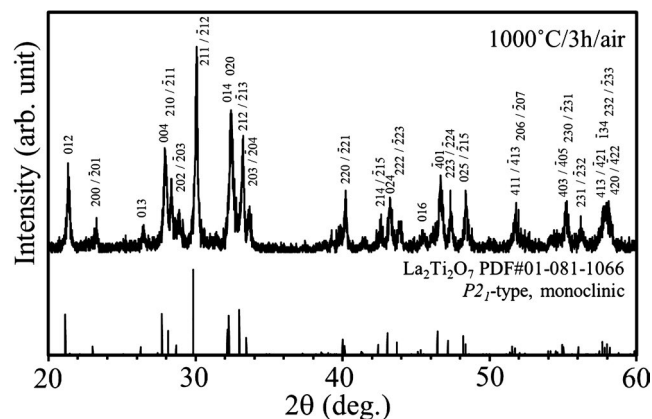


FIGURE 5 XRD pattern of NPs heat-treated at 1000°C/3 h/air

shown in Figure 7E,F, respectively. It can be seen that the high crystallinity with a regular array of lattice planes and no defects results following heat treatment.

The surface oxygen defect of the LF-FSP NPs and the NPs heat-treated at 1000°C/3 h/air was investigated by XPS analysis. Figure 8 provides the results around O1s region, showing the spectra at the binding energy of 529.5, 531.4, and 532.9 eV in the both samples. The binding energy at 529.5 eV is ascribed from O-Ti⁴⁺ in the crystal lattice and those at 531.4 and 532.9 eV are attributed to surface adsorbed hydroxyl groups.⁴⁶⁻⁴⁷ Considering that physically adsorbed hydroxyl groups on the samples must be eliminated in the ultrahigh vacuum condition of XPS apparatus, these signals can be said to be attributed to Ti-OH and H₂O, which are strongly bounded to surface defects.⁴⁷⁻⁴⁹ Figure 8 clearly reveals that the spectra at 531.4 and 532.9 eV in the LF-FSP NPs are higher than those in the NPs heat-treated at 1000°C/3 h/air, indicating the higher surface defect in the LF-FSP NPs.

The BET SSA for NPs heat-treated at 1000°C/3 h/air was 14 m²/g. Kim et al²⁷ reported synthesizing La₂Ti₂O₇ by a polymerizable complex (PC) and solid-state reaction (SSR) methods finding much lower SSAS of 5-8 m²/g from the PC method with heat treatment at 950-1050°C/2 h and after heat-treating at 1150°C/24 h to generate single phase materials with SSAs of 1 m²/g. We believe that the limited aggregation (low bulk density) of LF-FSP NPs (Figure 2A) likely suppresses necking, grain growth, and thus loss of surface area.

In addition to conventional spray pyrolysis, SSR, and PC methods, several other approaches to synthesize La₂Ti₂O₇ have been reported. Metallo-organic deposition³² yields highly aggregated powder. The flux method³⁶⁻³⁸ provides photocatalytically active, plate-like crystals but with large particle sizes (~μm). Hydrothermal synthesis produces thin nanosheets.^{33,34,39} The hydrothermal method is not suitable for mass production because of the times involved. Compared with the other methods,

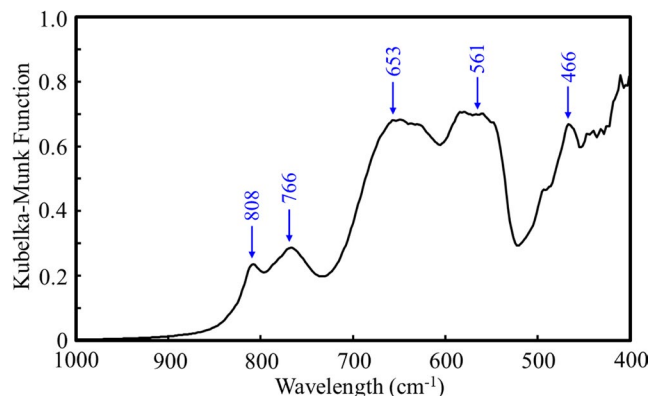


FIGURE 6 FTIR spectrum of NPs heat-treated at 1000°C/3 h/air [Color figure can be viewed at wileyonlinelibrary.com]

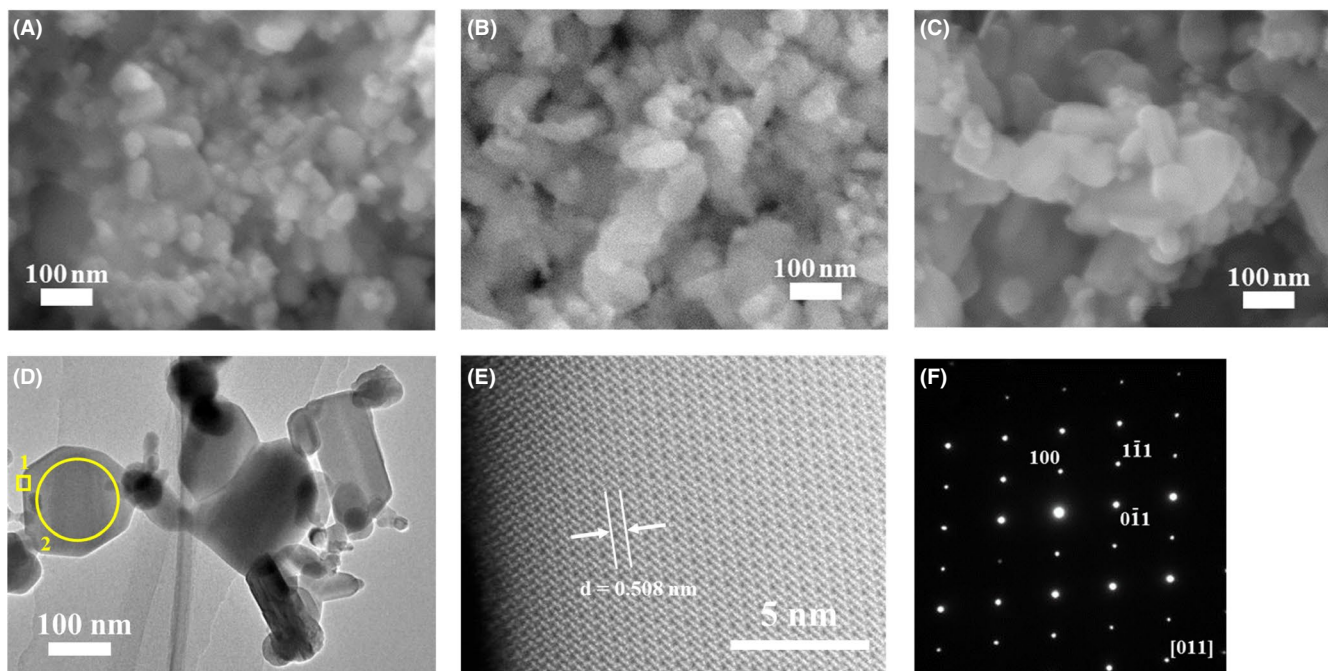


FIGURE 7 SEM images of NPs heat-treated at (A) 1000°C/1.5 h/air, (B) 1000°C/3 h/air and (C) 1000°C/6 h/air. (D) STEM image of NPs heat-treated at 1000°C/3 h/air. (E) HAADF-STEM image of area 1 in image (D) and (F) SAED of area 2 in image (D) [Color figure can be viewed at wileyonlinelibrary.com]

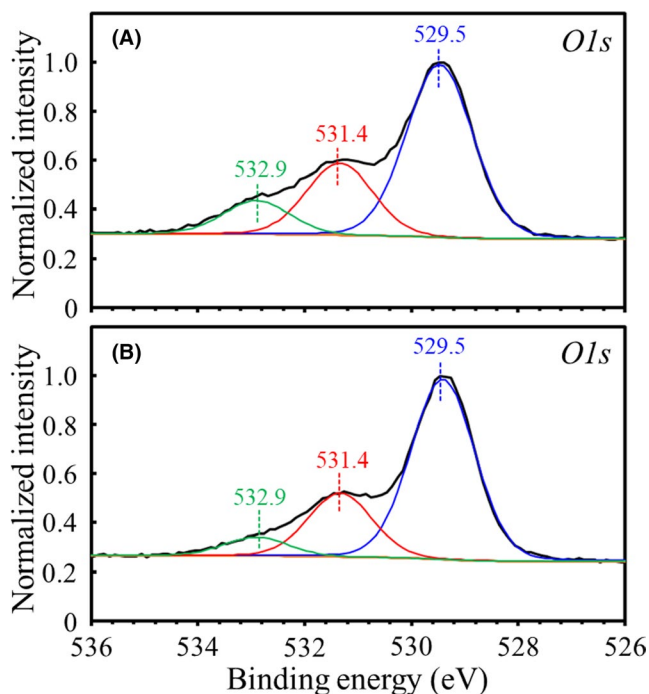


FIGURE 8 XPS of O1s region for (A) LF-FSP NPs and (B) NPs heat-treated at 1000°C/3 h/air [Color figure can be viewed at wileyonlinelibrary.com]

it can be said that LF-FSP offers characteristics of small plate-like $\text{La}_2\text{Ti}_2\text{O}_7$ NPs with high crystallinity and high SSAs.

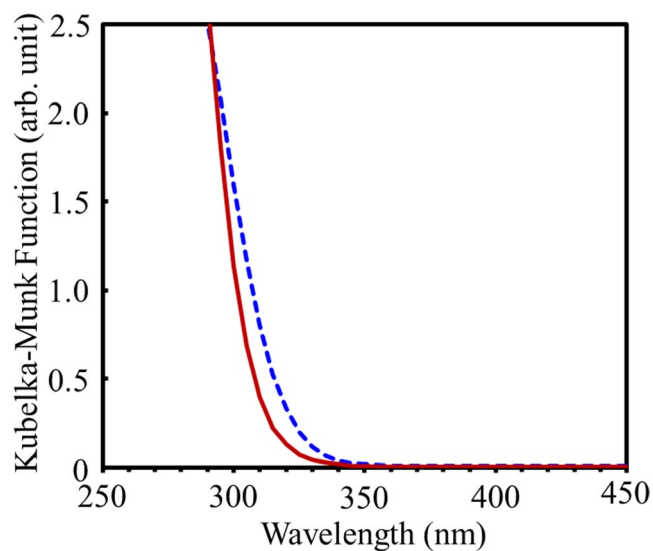


FIGURE 9 UV-vis diffused reflectance spectra of LF-FSP NP (blue dotted line) and that heat-treated at 1000°C/3 h/air (red solid line) [Color figure can be viewed at wileyonlinelibrary.com]

3.3 | Photocatalytic properties

Figure 9 provides the UV-vis diffuse reflectance spectra for LF-FSP NP (blue dotted line) and for NPs heat-treated at 1000°C/3 h/air (red solid line). The reflectance coefficient was converted to adsorption using the Kubelka-Munk function. The bandgap energy was estimated to be 3.87 eV for the

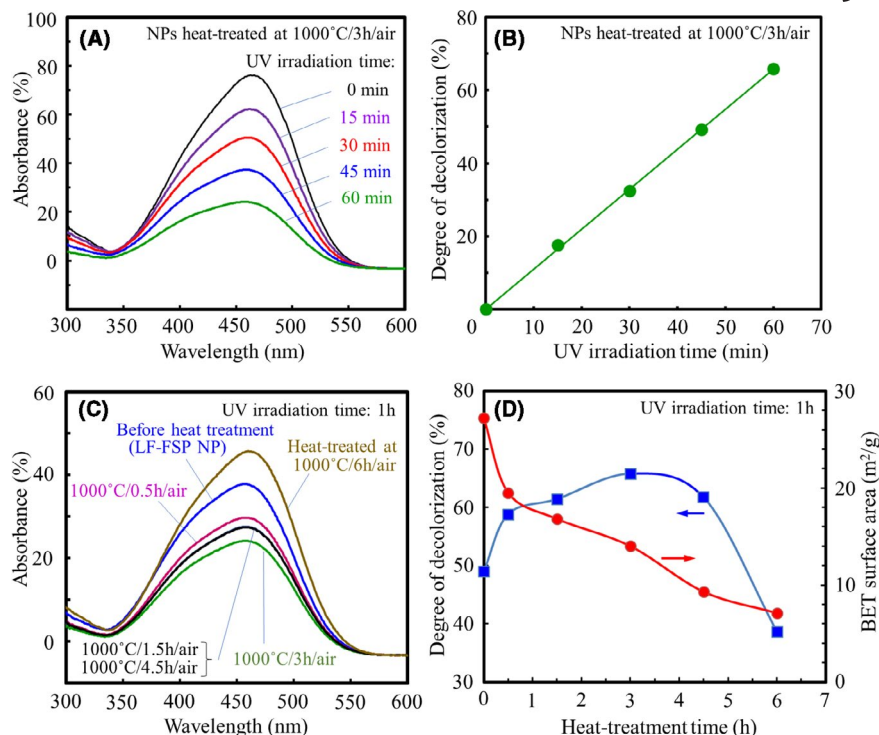


FIGURE 10 (A) Absorbance spectra of MO solution with NPs heat-treated at 1000°C/3 h/air after UV irradiation for different times. (B) Dependence of degree of decolorization on UV irradiation time for NPs heat-treated at 1000°C/3 h/air. (C) Absorbance spectra of MO solution without NPs and with NPs heat-treated at 1000°C/0-6 h/air after UV irradiation for 1 h. (D) Dependence of degree of decolorization and BET surface area on heat treatment time. Heat treatment was carried out at 1000°C/air. UV irradiation time was 60 min [Color figure can be viewed at wileyonlinelibrary.com]

LF-FSP NPs and 4.00 eV for the heat-treated ones from the absorption edges. These values are in good agreement with those reported previously.²²⁻²⁵ Therefore, we confirm that the samples readily absorb UV light.

Dai et al⁵⁰ reported that mesoporous titania NPs cause photocatalytic decomposition of the MO in water under UV irradiation leading to decolorization of the MO solutions. Thus, quantitative evaluation of the photocatalytic activity can be carried out by measuring decolorization of MO solutions with the photocatalyst under UV irradiation. Since MO has good resisting property toward the UV light, use of it has an advantage to evaluate photocatalytic activity of catalysts under the UV irradiation precisely.

Figure 10A shows the absorbance spectra of an MO solution with NPs heat-treated at 1000°C/3 h/air after UV irradiation for different times (0-60 min). The MO concentration (C) after irradiation was estimated from the absorbance at 464 nm and the decolorization degree $((C_0 - C) / C_0) \times 100$ (%), C_0 : initial MO concentration) was calculated. Figure 10B provides a dependence of the decolorization degree on UV irradiation time for NPs heat-treated at 1000°C/3 h/air. It can be seen that the decolorization degree increases monotonically with increases in irradiation time. Next, we examined the catalytic activity of the NPs heat-treated at 1000°C for different times (0-6 hours) in air

by using the decolorization of the MO solution. Figure 10C provides absorbance spectra of the MO solution after UV irradiation with LF-FSP NP and NPs heat-treated at 1000°C/0.5-6 h/air. The UV irradiation time was 1 hour. Similarly, the decolorization degree of MO, which implies the photocatalytic activity in this case, was evaluated from the spectra, and their dependences on the heat treatment time were derived, which is shown in Figure 10D. This figure also provides a dependence of BET SSAS of NPs and heat-treating time. In the figure, the data at 0 hour are for the LF-FSP NPs. Although the BET surface area decreased monotonically with the heat-treating time, the highest photocatalytic activity was obtained at 3 hours. For heat-treating times shorter than 3 hours, the BET surface area decreased while the photocatalytic activity increased. Yan et al⁴⁹ described that the surface defects of TiO₂, that is, oxygen vacancy clusters, could promote the separation of electron-hole pairs under irradiation, which leads to enhancement of the photocatalytic activity. As described above, the surface defect evaluated from XPS of O1s in the LF-FSP NPs decreased by the heat-treating at 1000°C/3 h/air. Therefore, it can be said that the surface defect is not dominant for the photocatalytic activity as for our samples. The reason might be due to improvements in the crystallinity and interior defect density reductions.⁴²

Improvement in the crystallinity enhances the mobility of electrons and holes and reduction in the defect suppresses recombination of electrons and holes.

In contrast, in the range of the heat-treating times longer than 3 hours, photocatalytic activity decreased monotonically with time. This might arise from decreases in surface area. Therefore, best photocatalytic activity could be obtained from NPs heat-treated at 1000°C/3 h/air, which still offer large surface area of 14 m²/g.

4 | CONCLUSIONS

In this study, perovskite-slab-type La₂Ti₂O₇ NPs were synthesized using LF-FSP of metallo-organic precursors of lanthanum isobutyrate and triethanolamine titanate coupled with a subsequent heat treatment at 1000°C/air. The LF-FSP NPs had characteristically low agglomeration of primary particles with APSs of 26 nm and large SSAs of 27 m²/g. Heat treatment at 1000°C/3 h/air resulted in formation of plate-like single crystal NPs while still retaining SSAs of 14 m²/g and eliminating microstructural defects thereby optimizing photocatalytic activity. Finally, this work introduces LF-FSP processing of perovskite-slab-type NPs with high crystallinity and high surface area for photocatalytic applications.

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REFERENCES

- Bickmore CR, Waldner KF, Baranwal R, Hinklin T, Treadwell DR, Laine RM. Ultrafine titania by flame spray pyrolysis of a titanatane complex. *J Euro Ceram Soc.* 1998;18(4):287–97.
- Laine RM, Marchal JC, Sun HP, Pan XQ. Nano- α -Al₂O₃ by liquid-feed flame spray pyrolysis. *Nat Mater.* 2006;5:710–2.
- Messing GL, Zhang S-C, Jayanthi GV. Ceramic powder synthesis by spray pyrolysis. *J Am Ceram Soc.* 1993;76(11):2707–26.
- Hinklin T, Toury B, Gervais C, Babonneau F, Gislason JJ, Morton RW, et al. Liquid-feed flame spray pyrolysis of metalloorganic and inorganic alumina sources in the production of nanoalumina powders. *Chem Mater.* 2004;16(1):21–30.
- Yi E, Wang W, Kieffer J, Laine RM. Flame made nanoparticles permit processing of dense, flexible, Li⁺ conducting ceramic electrolyte thin films of cubic-Li₇La₃Zr₂O₁₂ (c-LLZO). *J Mater Chem A.* 2016;4(33):12947–54.
- Yi E, Wang W, Kieffer J, Laine RM. Key parameters governing the densification of cubic-Li₇La₃Zr₂O₁₂ Li⁺ conductors. *J Power Sources.* 2017;352(1):156–64.
- Yi E, Temeche E, Laine RM. Superionically conducting β'' -Al₂O₃ thin films processed using flame synthesized nanopowders. *J Mater Chem A.* 2018;6(26):12411–9.
- Abe Y, Yi E, Laine RM. Processing thin, dense, transparent Ce:Y₃Al₅O₁₂ films from flame made nanopowders for white light applications. *J Euro Ceram Soc.* 2019;39(15):4972–8.
- Bednorz JG, Müller KA. Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z Physik B.* 1986;64:189–93.
- Wu MK, Ashburn JR, Torng CJ, Hor PH, Meng RL, Gao L, et al. Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. *Phys Rev Lett.* 1987;58(9):908–10.
- Mulder AT, Benedek NA, Rondinelli JM, Fennie CJ. Turning ABO₃ antiferroelectrics into ferroelectrics: design rules for practical rotation-driven ferroelectricity in double perovskites and A₃B₂O₇ Ruddlesden-Popper compounds. *Adv Fun Mater.* 2013;23(38):4810–20.
- Amanuma K, Hase T, Miyasaka Y. Preparation and ferroelectric properties of SrBi₂Ta₂O₉ thin films. *Appl Phys Lett.* 1995;66(2):221–3.
- Mao X, Wang W, Chen X, Lu Y. Multiferroic properties of layer-structured Bi₅Fe_{0.5}Co_{0.5}Ti₃O₁₅. *Appl Phys Lett.* 2009;95:082901/1–3.
- Keeney L, Maity T, Schmidt M, Amann A, Deepak N, Petkov N, et al. Magnetic field-induced ferroelectric switching in multiferroic aurivillius phase thin films at room temperature. *J Am Ceram Soc.* 2013;96(8):2339–57.
- Shimizu K, Itoh S, Hatamachi T, Kodama T, Sato M, Toda K. Photocatalytic water splitting on Ni-intercalated Ruddlesden–Popper tantalate H₂La_{2/3}Ta₂O₇. *Chem Mater.* 2005;17(20):5161–6.
- Machida M, Yabunaka J, Kijima T. Synthesis and photocatalytic property of layered perovskite tantalates, RbLnTa₂O₇ (Ln = La, Pr, Nd, and Sm). *Chem Mater.* 2000;12(3):812–7.
- Ispov VA. Crystal chemical aspects of the layered perovskite-like oxide ferroelectrics of the AnMnO_{3n2} type. *Ferroelectrics.* 1999;220(1):79–103.
- Lichtenberg F, Herrnberger A, Wiedenmann K, Mannhart J. Synthesis of perovskite-related layered A_nB_nO_{3n+2} = ABO_x type niobates and titanates and study of their structural, electric and magnetic properties. *Progress in Solid State Chem.* 2001;29(1–2):1–70.
- Nanamatsu S, Kimura M, Doi K, Matsushita S, Yamada N. A new ferroelectric: La₂Ti₂O₇. *Ferroelectrics.* 1974;8(1):511–3.
- Stefanovich SY, Nanamatsu S, Venetsev YN. Photovoltaic properties and photoconductivity of A₂B₂O₇ ferroelectrics. *Ferroelectrics.* 1980;29(1):59–62.
- Yamamoto JK, Bhalla AS. Piezoelectric properties of layered perovskite A₂Ti₂O₇ (A=La and Nd) single-crystal fibers. *J Appl Phys.* 1991;70(8):4469–71.
- Hwang DW, Lee JS, Li W, Oh SH. Electronic band structure and photocatalytic activity of Ln₂Ti₂O₇ (Ln = La, Pr, Nd). *J Phys Chem B.* 2003;107(21):4963–70.
- Uno M, Kosuga A, Okui M, Horisaka K, Yamanaka S. Photoelectrochemical study of lanthanide titanium oxides, Ln₂Ti₂O₇ (Ln = La, Sm, and Gd). *J Alloys Comp.* 2005;400(1–2):270–5.
- Abe R, Higashi M, Sayama K, Abe Y, Sugihara H. Photocatalytic activity of R₃MO₇ and R₂Ti₂O₇ (R = Y, Gd, La; M = Nb, Ta)

- for water splitting into H₂ and O₂. *J Phys Chem B*. 2006;110(5):2219–26.
25. Wang Z, Teramura K, Hosokawa S, Tanaka T. Photocatalytic conversion of CO₂ in water over Ag-modified La₂Ti₂O₇. *Appl Cat B: Environ*. 2015;163:241–7.
26. Kim HG, Hwang DW, Kim J, Kim YG, Lee JS. Highly donor-doped (110) layered perovskite materials as novel photocatalysts for overall water splitting. *Chem Commun*. 1999;12:1077–8.
27. Kim HG, Hwang DW, Bae SW, Jung JH, Lee JS. Photocatalytic water splitting over La₂Ti₂O₇ synthesized by the polymerizable complex method. *Catal Lett*. 2003;91(3–4):193–8.
28. Ku Y, Wang LC, Ma CM. Photocatalytic oxidation of isopropanol in aqueous solution using perovskite – structured La₂Ti₂O₇. *Chem Eng Technol*. 2007;30(7):895–900.
29. Hou WM, Ku Y. Synthesis and characterization of La₂Ti₂O₇ employed for photocatalytic degradation of reactive red 22 dyestuff in aqueous solution. *J Alloys Comp*. 2011;509(19):5913–8.
30. Rahimi-Nasrabadi M, Mahdavi S, Adib K. Photocatalytically active La₂Ti₂O₇ nanostructures, synthesis and characterization. *J Mater Sci: Mater Electron*. 2017;28(17):12564–71.
31. Rugen EE, Koczur KM, Skrabalak SE. Facile synthesis of porous La-Ti-O and LaTiO₂N microspheres. *Dalton Trans*. 2017;46(32):10727–33.
32. Zhao Z, Zhang Y, Yang J, Li H, Song W, Zhao X. Low-temperature synthesis of La₂Ti₂O₇ nanocrystal by metallorganic decomposition method. *J Ceram Soc Jpn*. 2005;113(1313):67–70.
33. Chen D, Xu R. Hydrothermal synthesis and characterization of La₂M₂O₇ (M= Ti, Zr) powders. *Mater Res Bull*. 1998;33(3):409–17.
34. Li KW, Wang Y, Wang H, Zhu M, Yan H. Hydrothermal synthesis and photocatalytic properties of layered La₂Ti₂O₇ nanosheets. *Nanotechnology*. 2006;17(19):4863–7.
35. Onozuka K, Kawakami Y, Imai H, Yokoi T, Tatsumi T, Kondo JN. Perovskite-type La₂Ti₂O₇ mesoporous photocatalyst. *J Solid State Chem*. 2012;192:87–92.
36. Arney D, Porter B, Greve B, Maggard PA. New molten-salt synthesis and photocatalytic properties of La₂Ti₂O₇ particles. *J Photochem Photobiol A: Chem*. 2008;199(2–3):230–5.
37. Hojamberdiev M, Yamaguchi A, Yubuta K, Oishi S, Teshima K. Fabrication of La₂Ti₂O₇ crystals using an alkali-metal molybdate flux growth method and their nitridability to form LaTiO₂N crystals under a high-temperature NH₃ atmosphere. *Inorg Chem*. 2015;54(7):3237–44.
38. Wagata H, Zettsu N, Yamaguchi A, Nishikiori H, Yabuta K, Oishi S, et al. Chloride flux growth of La₂Ti₂O₇ crystals and subsequent nitridation to form LaTiO₂N crystals. *Cryst Growth Des*. 2015;15(1):124–8.
39. Meng F, Hong Z, Arndt J, Li M, Zhi M, Yang F, et al. Visible light photocatalytic activity of nitrogen-doped La₂Ti₂O₇ nanosheets originating from band gap narrowing. *Nano Res*. 2012;5(3):213–21.
40. Fuierer PA, Newnham RE. La₂Ti₂O₇ Ceramics. *J Am Ceram Soc*. 1991;74(11):2876–81.
41. Ishizawa N, Marumo F, Iwai S, Kimura M, Kawamura T. Compounds with perovskite-type slabs. V. A high-temperature modification of La₂Ti₂O₇. *Acta Cryst*. 1982;B38(2):368–72.
42. Maeda K, Domen K. New non-oxide photocatalysts designed for overall water splitting under visible light. *J Phys Chem C*. 2007;111(22):7851–61.
43. Chen D, Jiao X, Xu R. Hydrothermal synthesis and characterization of the layered titanates MLaTiO₄ (M= Li, Na, K) powders. *Mater Res Bull*. 1999;34(5):685–91.
44. Last JT. Infrared-absorption studies on barium titanate and related materials. *Phys Rev*. 1957;105(6):1740–50.
45. Kartha K, Pai MR, Banerjee AM, Pai RV, Meena SS, Bharadwaj SR, et al. Modified surface and bulk properties of Fe-substituted lanthanum titanates enhances catalytic activity for CO⁺ N₂O reaction. *J Molecular Catalyst A: Chemical*. 2011;335(1–2):158–68.
46. Feng W, Wu G, Li L, Guan N. Solvent-free selective photocatalytic oxidation of benzyl alcohol over modified TiO₂. *Green Chem*. 2011;13(11):3265–72.
47. Iwabuchi A, Choo C, Tanaka K. Titania nanoparticles prepared with pulsed laser ablation of rutile single crystals in water. *J Phys Chem B*. 2004;108(30):10863–71.
48. Wang R, Sakai N, Fujishima A, Watanabe T, Hashimoto K. Studies of surface wettability conversion on TiO₂ single-crystal surfaces. *J Phys Chem B*. 1999;103(12):2188–94.
49. Yan J, Wu G, Guan N, Li L, Li Z, Cao X. Understanding the effect of surface/bulk defects on the photocatalytic activity of TiO₂: anatase versus rutile. *Phys Chem Chem Phys*. 2013;15(26):10978–88.
50. Dai K, Chen H, Peng T, Ke D, Yi H. Photocatalytic degradation of methyl orange in aqueous suspension of mesoporous titania nanoparticles. *Chemosphere*. 2007;69(9):1361–7.

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