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Photocatalytic Hydrogen Evolution Using Activated Carbon Supported LaFeO3

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Abstract
Photocatalytic hydrogen production represents a sustainable approach to addressing energy demands while simultaneously mitigating environmental pollution. In this study, activated carbon-supported LaFeO3 (AC-LaFeO3) was synthesized and applied as a photocatalyst for hydrogen evolution from the oxytetracycline (OTC) solution as a model pollutant and sacrificial agent. Comprehensive characterization techniques, such as SEM, BET, X-ray diffraction (XRD), and photoluminescence (PL) spectroscopy, confirmed the morphological and optical properties of AC-LaFeO3. It demonstrated enhanced photocatalytic performance under visible light irradiation, attributed to the synergistic effects between LaFeO3 and activated carbon, including improved charge separation and increased surface area. The hydrogen evolution rate reached a maximum of 142 mmol/h under optimized conditions after 4 h of reaction duration. The results highlight the potential of AC-LaFeO3 in simultaneously addressing wastewater treatment challenges and sustainable hydrogen production, providing a dual-purpose solution for environmental remediation and clean energy generation.

Research Article

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1. Introduction

Hydrogen energy is widely recognized as a promising alternative to conventional fossil fuels, offering a clean and sustainable energy source. Among the various methods for hydrogen generation, photocatalytic water splitting under visible light irradiation has emerged as one of the most efficient and environmentally friendly approaches. The performance of photocatalysts is influenced by critical factors such as light absorption, charge separation efficiency, and surface area, all of which directly impact their hydrogen production capabilities (Arabacı et al., 2024; Bakır and Orak, 2024; Bakır et al., 2024; Haste et al., 2024; Horoz et al., 2024; Orak, 2024b; Orak et al., 2024). Recently, perovskite oxide-based photocatalysts, such as $LaFeO_3$, have gained considerable attention due to their excellent stability, non-toxicity, and potential for efficient photocatalytic water splitting. However, the inherent limitations of $LaFeO_3$ in terms of low electron mobility and poor charge separation necessitate the development of composite materials to enhance its photocatalytic performance (Orak and Yüksel, 2021; Orak and Yüksel, 2021; Orak and Yüksel, 2022b, 2022a; Orak and Yüksel, 2022). To address these challenges, the development of composite materials has become a focal point of research. Activated carbon (AC), with its high surface area, abundant porosity, and excellent electrical conductivity, has been widely used as a support material in various catalytic and photocatalytic applications (Batur et al., 2022; Batur et al., 2023; Batur et al., 2023). By combining AC with $LaFeO_3$, the photocatalytic efficiency of $LaFeO_3$ can be enhanced through improved charge transfer, increased surface area, and the formation of synergetic effects (Monser and Adhoum, 2009; Ribas et al., 2020). Therefore, this combination leverages the strengths of both materials, positioning the activated carbon supported $LaFeO_3$ (AC-$LaFeO_3$) composites as promising candidates for photocatalytic applications. In parallel, the management of pharmaceutical pollutants in water bodies has emerged as a pressing global concern. Oxytetracycline (OTC), a broad-spectrum antibiotic widely used in veterinary and human medicine, is one such pollutant frequently detected in wastewater. Due to its high solubility and stability, OTC persists in aquatic environments, posing risks to ecosystems and contributing to the development of antibiotic resistance (Orak, 2024a; Orak and Ersöz, 2024). Conventional wastewater treatment methods often fail to effectively degrade such complex organic compounds, necessitating advanced approaches for simultaneous degradation and resource recovery (Ren et al., 2020; Esmaeili et al., 2023; Li et al., 2024). Photocatalytic processes offer a dual-purpose solution to these challenges by enabling the degradation of OTC while concurrently generating hydrogen as a clean energy source. In this context, AC-$LaFeO_3$ composite have emerged as efficient photocatalysts, capable of utilizing visible-light energy for both OTC degradation and hydrogen production. This study aims to develop and evaluate an AC-$LaFeO_3$ composite for photocatalytic hydrogen production using OTC solution as both a model pollutant and a sacrificial agent. By investigating the structural, optical, and catalytic properties of AC-$LaFeO_3$, this research seeks to establish a comprehensive understanding of its potential for addressing the dual challenges of energy sustainability and environmental remediation.

2. Materials and Methods

2.1 Synthesis of AC-$LaFeO_3$ composite

AC-$LaFeO_3$ composite catalyst with 10 wt% $LaFeO_3$ was synthesized using a sol-gel citrate method. Specifically, 0.35 g of

$La(NO_3)_3 \cdot 6H_2O$, 0.32 g of $Fe(NO_3)_3 \cdot 9H_2O$, and 0.5 g of citric acid were dissolved in 100 mL of distilled water. AC (1.8 g) was introduced into the solution, followed by 30 min of sonication to disperse the carbon particles. The solution was then stirred and heated at 80 °C until a gel formed. This gel was dried at 120 °C for 3 h. Afterward, the dried material was ground into a powder and calcined at 300 °C for 3 h to obtain the AC-$LaFeO_3$ composite.

2.2 Characterization

The structural properties of the $LaFeO_3$ and $LaFeO_3$/AC composite were analyzed using X-ray diffraction (XRD, Rigaku X-ray diffractometer) to confirm the crystalline phase. Their surface morphology was observed using scanning electron microscopy (SEM, FEI QUANTA 250 FEG). Surface areas were determined using BET (NOVA 2200E BET Surface Area Analyzer) analysis. The optical properties were studied using the photoluminescence (PL, Edinburgh Instruments FLSP920 Fluorescence Spectrometer) spectroscopy.

2.3 Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution was carried out using OTC solution (20 ppm, 200 mL) under visible light irradiation using a 300 W xenon lamp. In this context, the impact of key reaction parameters (pH (3-7) and catalyst amount (0-0.5 g/L) was investigated. The amount of evolved hydrogen during the experiments was measured using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

3. Results and Discussion

3.1. Characterization study

SEM images were obtained to evaluate the morphology of the $LaFeO_3$ and AC-$LaFeO_3$ composite. Figure 1a shows the SEM image of $LaFeO_3$, which consists of irregularly shaped nanoparticles with a size range of 30–50 nm. In contrast, the AC-$LaFeO_3$ composite (Figure 1b) exhibits a uniform distribution of $LaFeO_3$ on the surface of AC. The high dispersion of $LaFeO_3$ on AC is expected to enhance its photocatalytic efficiency by increasing the surface area and providing more active sites for hydrogen evolution. Similar results were reported in the literature (Iervolino et al., 2016; Shabbir et al., 2006; Acharya et al., 2020).

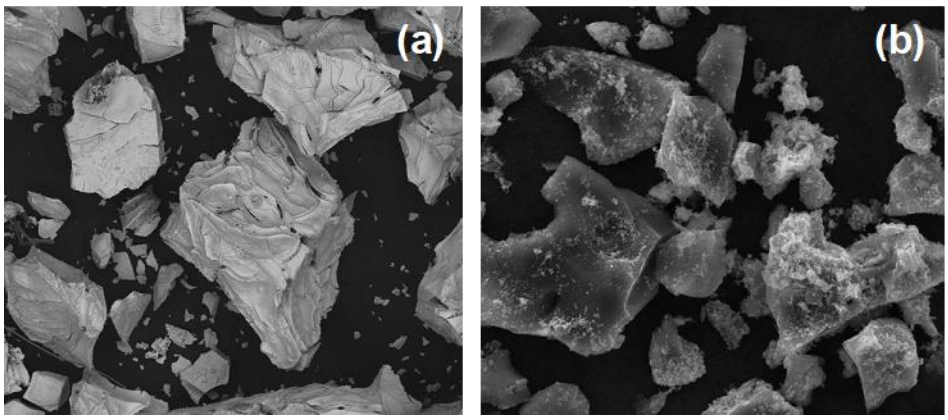

Figure 1. SEM images of $LaFeO_3$ (a) and AC-$LaFeO_3$ composite (b)

In addition, the BET surface area of $LaFeO_3$ and AC-$LaFeO_3$ composite were analyzed, and the surface area of pure $LaFeO_3$ was found to be 29.8 m^2/g, whereas AC-$LaFeO_3$ composite exhibited significantly higher surface area (198.2

m^2/g). This increase in the BET surface area is due to the porous structure of AC, which provides additional active sites for the photocatalytic reaction. The XRD patterns of pristine $LaFeO_3$ and the AC-$LaFeO_3$ composite are shown in Figure 2. The diffraction peaks at 2θ = 22.63°, 32.22°, 39.73°, 46.21°, 57.45°, 67.42°, 72.12°, and 76.69° correspond to the characteristic reflections of the $LaFeO_3$ perovskite structure (Yang et al., 2007; Abazari and Sanati, 2013; Rusevova et al., 2014; Xu et al., 2020). No significant shift in the peaks of the AC-$LaFeO_3$ composite was observed, indicating that the crystalline structure of $LaFeO_3$ was not significantly altered by the incorporation of AC. Additionally, no peaks from AC were observed, suggesting that the AC support did not interfere with the crystalline phase of $LaFeO_3$.

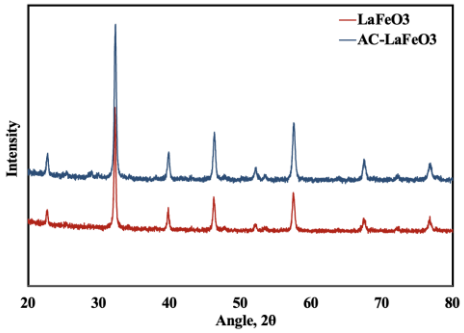

Figure 2. XRD patterns of pristine $LaFeO_3$ and the AC-$LaFeO_3$ composite

The photoluminescence (PL) spectra of pristine $LaFeO_3$ and the AC-$LaFeO_3$ composite were recorded to investigate the charge carrier recombination rates. Figure 3 shows the PL spectra of pristine $LaFeO_3$ and the AC-$LaFeO_3$ composite and the pristine $LaFeO_3$ exhibited a strong PL emission peak around 550 nm, which is indicative of significant electron-hole recombination (Hussain et al., 2013; Rusevova et al., 2014; Iervolino et al., 2017). In contrast, the AC-$LaFeO_3$ composite exhibited weaker PL emission, suggesting that the incorporation of AC effectively suppressed electron-hole recombination. This reduction in recombination is expected to improve the photocatalytic performance of the composites.

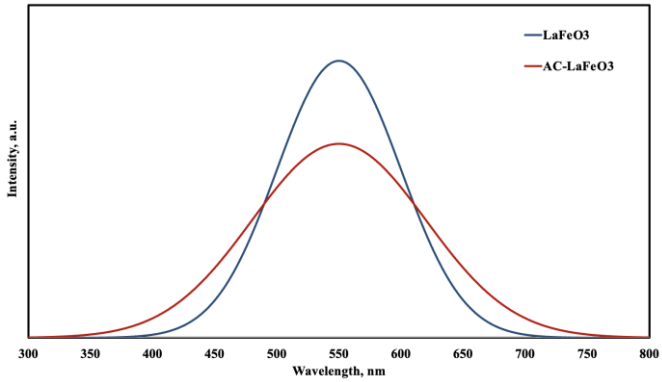

Figure 3. PL spectra of pristine $LaFeO_3$ and AC-$LaFeO_3$ composite.

3.3 Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution experiments were carried out to evaluate the activity of the synthesized AC-$LaFeO_3$ composite under different reaction conditions. The experimental results demonstrated that the hydrogen evolution rate is significantly influenced by pH and catalyst amount. The photocatalytic activity was examined over a range of pH values. The results revealed that the hydrogen evolution efficiency increased with a decrease in pH, reaching a maximum at acidic conditions (pH = 3). This behavior can be attributed to the enhanced photocatalytic efficiency of the AC-$LaFeO_3$ composite in acidic environments, which promotes charge separation and minimizes recombination. However, at higher pH values, a decline in hydrogen evolution was observed due to reduced proton availability and the competitive adsorption of hydroxide ions. The catalyst amount is another pivotal factor in photocatalytic hydrogen evolution from OTC solution. Experiments were conducted by varying the catalyst amount from 0 g/L to 0.5 g/L. The results indicated that increasing the catalyst amount enhances the active surface area available for photocatalytic reactions, thereby improving hydrogen evolution. The highest hydrogen evolution (~142 mmol/g) was obtained at pH 3 using 0.5 g/L of AC-$LaFeO_3$ composite for 4 h.

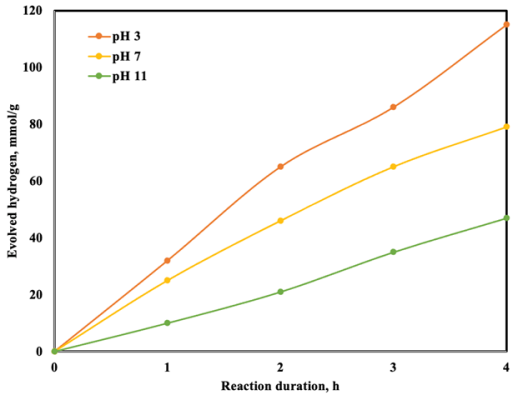

Figure 4. The impact of pH on photocatalytic hydrogen evolution from OTC solution

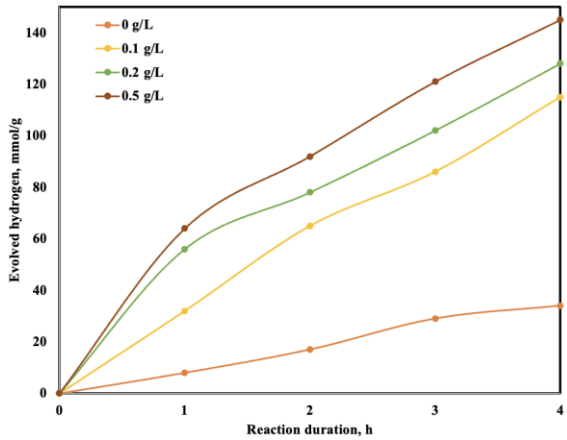

Figure 5. The impact of catalyst amount on photocatalytic hydrogen evolution from OTC solution.

In the literature, Iervolino et al. reported 113 mmol/g for hydrogen production from glucose using Ru-doped $LaFeO_3$ under visible light irradiation for 5 hours, at pH 4 (Iervolino et al., 2017). Acharya et al. observed 75 mmol/g for hydrogen evolution using $LaFeO_3$ nanospheres with RGO (reduced graphene oxide) under visible light for 6 hours at pH 7 (Acharya et al., 2020a). The findings suggests that the AC-$LaFeO_3$ composite provides a higher rate of hydrogen production under slightly more acidic conditions. Ribas et al. studied the photocatalytic hydrogen evolution using $LaFeO_3$ at different pH levels and found that the optimal hydrogen evolution occurred at pH 3 (Ribas et al., 2020), similar to this study. It shows the robustness of $LaFeO_3$-based photocatalysts under acidic conditions. Therefore, AC-$LaFeO_3$ composite is effective under acidic conditions to produce hydrogen from OTC solution under visible light.

Conclusion

AC-$LaFeO_3$ composite was synthesized via sol-gel to use photocatalytic hydrogen evolution from OTC solution. The results of characterization study proved its successful synthesis. AC-$LaFeO_3$ composite exhibits significantly enhanced hydrogen evolution performance compared to pristine $LaFeO_3$. The improvement is attributed to the synergistic effects between $LaFeO_3$ and AC, which increase the surface area, improve charge separation, and enhance light absorption. This study highlights the potential of AC-$LaFeO_3$ composite as efficient photocatalysts for hydrogen production, with promising applications in renewable energy generation.

References

Abazari, R., Soheila, S., 2013. Perovskite LaFeO3 nanoparticles synthesized by the reverse microemulsion nanoreactors in the presence of aerosol-ot: morphology, crystal structure, and their optical properties. *Superlattices and Microstructures*, 64: 148–57.

Acharya, S., Padhi, D.K., Parida, K.M., 2020. Visible light driven LaFeO3 Nano Sphere/RGO composite photocatalysts for efficient water decomposition reaction. *Catalysis Today*, 353: 220–31.

Arabacı, B., Bakır, R., Orak, C., Yüksel, A., 2024. Integrating experimental and machine learning approaches for predictive analysis of photocatalytic hydrogen evolution using Cu/g-C3N4." *Renewable Energy*, 237: 121737.

Bakır, R., Orak, C., 2024. Stacked machine learning approach for predicting evolved hydrogen from sugar ındustry wastewater. *International Journal of Hydrogen Energy*, 85: 75–87.

Bakır, R., Orak, C., Yüksel, A., 2024. A machine learning ensemble approach for predicting solar-sensitive hybrid photocatalysts on hydrogen evolution. *Physica Scripta*, 99(7): 076015.

Batur, E., Baytar, O., Horoz, S., Şahin, Ö., Kutluay, S., 2022. Enhancement in ıncident photon-to-current conversion efficiency of manganese-decorated activated carbon-supported cadmium sulfide nanocomposite. *Journal of Materials Science: Materials in Electronics*, 33(20): 16286–96.

Batur, E., Kutluay, S., Baytar, O., Şahin, Ö., Horoz, S., 2023. Superior incident photon-to-current conversion efficiency of mo-doped activated carbon supported CdS-sensitized solar cells. *Environmental Science and Pollution Research International*, 30(8): 19766–75.

Batur, E., Şahin, Ö., Baytar, O., Horoz, S., Kutluay. S., 2023. High solar cell efficiency of lanthanum-alloyed activated carbon–supported cadmium sulfide as a promising semiconductor nanomaterial. *Journal of the Australian Ceramic Society*, 59(1): 9–18.

Esmaeili, A., Shideh P.H.K., Azadeh E.P., Fatemeh E.K.S., Ali E.P., Ali D., Fatemeh-Sadat T.Y., 2023. CdS nanocrystallites sensitized ZnO nanosheets for visible light ınduced sonophotocatalytic/photocatalytic degradation of tetracycline: from experimental results to a generalized model based on machine learning methods. *Chemosphere*, 332: 138852.

Haste, Z.Ö., Horoz, S., Orak, C., Biçer, E., 2024. Green-Synthesized SnO2 derived from kombucha tea and assessment of ıts photocatalytic activity for the degradation of procion red MX-5B. *ChemistrySelect*, 9(43): e202403264.

Horoz, S., Orak, C., Biçer, E., 2024. Green Synthesis of ZnO and Ni-Doped ZnO from okra stalks for the photocatalytic degradation of procion red MX-5B." *International Journal of Phytoremediation*.

Hussain, T., Saadat A. Siddiqi, S.A., Awan, M.S., 2013. Induced modifications in the properties of sr doped BiFeO3 multiferroics. *Progress in Natural Science: Materials International* 23(5): 487–92.

Iervolino, G., Vaiano, V., Sannino, D., Rizzo, L., Ciambelli, P., 2016. Production of hydrogen from glucose by LaFeO3 based photocatalytic process during water treatment. *International Journal of Hydrogen Energy*, 41(2): 959–66.

Iervolino, G., Vaiano, V., Sannino, D., Rizzo, L., Palma, V., 2017., Enhanced photocatalytic hydrogen production from glucose aqueous matrices on ru-doped LaFeO3. *Applied Catalysis B: Environmental* 207:182–94.

Li, Y., Guangyi, Z., Danxin, L., Xiaoqin, W., Haifeng, G., 2024. Tetracycline hydrochloride degradation in polarity ınverted microbial fuel cells: performance, mechanisms and microbiology. *Chemosphere*, 349:140902.

Monser, L., Nafaâ, A., 2009. Tartrazine modified activated carbon for the removal of Pb(II), Cd(II) and Cr(III). *Journal of Hazardous Materials*, 161(1): 263–69.

Orak, C., 2024a. Application of response surface methodology for bioenergy generation in a yeast-based microbial fuel cell. *RSC Advances* 14(46): 34356–61.

Orak, C., 2024b. Enhanced degradation of procion red MX-5B using Fe-Doped Corn Cob Ash and Fe-Doped g-C3N4. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 46(1):14244–58.

Orak, C., Gülin E., 2024. Heterogeneous photo-fenton-like degradation of oxytetracycline containing wastewater. *Journal of Advanced Research in Natural and Applied Sciences*, 10(1): 182–89.

Orak, C., Oğuz, T., Horoz, S., 2024. Facile synthesis of mn-doped cds nanoparticles on carbon quantum dots: towards efficient photocatalysis. *Journal of the Australian Ceramic Society*.

Orak, C., Yüksel, A., 2021. Graphene-Supported LaFeO3 for photocatalytic hydrogen energy production. *International Journal of Energy Research*, 45(9): 12898–914.

Orak, C., Yüksel, A., 2021. Photocatalytic hydrogen energy evolution from sugar beet wastewater. *ChemistrySelect*, 6(43): 12266–75.

Orak, C., Yüksel, A., 2022. Box-Behnken design for hydrogen evolution from sugar ındustry wastewater using solar-driven hybrid catalysts. *ACS Omega*, 7(46): 42489–98.

Orak, C., Yüksel, A., 2022a. Box–Behnken design for hydrogen evolution from sugar ındustry wastewater using solar-driven hybrid catalysts. *ACS Omega* 7(46): 42489–98.

Orak, C., Yüksel, A., 2022b. Comparison of photocatalytic performances of solar-driven hybrid catalysts for hydrogen energy evolution from 1,8–diazabicyclo[5.4.0]Undec-7-Ene (DBU) solution. *International Journal of Hydrogen Energy*, 47(14): 8841–57.

Ren, Z., Fangyuan C., Kangxin W., Jinfeng L., 2020. Enhanced photocatalytic activity for tetracyclines degradation with ag modified G-C3N4 composite under visible light. *Journal of Photochemistry and Photobiology A: Chemistry*, 389.

Ribas, M.C., De Franco, M.A., Adebayo, M.A., Lima, E.C., Parkes, G., Feris, L.A., 2020. Adsorption of Procion Red MX-5B dye from aqueous solution using homemade peach and commercial activated carbons. *Applied Water Science*, 10(6): 1-13.

Rusevova, K., Köferstein, R., Rosell, M., Richnow, H.H., Kopinke, F.D., Georgi, A., 2014. LaFeO3 and BiFeO3 perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions. *Chemical Engineering Journal*, 239: 322-331.

Shabbir, G., Qureshi, A.H., Saeed, K., 2006. Nano-Crystalline LaFeO3 powders synthesized by the citrate-gel method. *Materials Letters*, 60(29–30): 3706–9.

Xu, K., Yang, X., Ruan, L., Qi, S., Liu, J., Liu, K., ... Feng, J., 2020. Superior adsorption and photocatalytic degradation capability of mesoporous LaFeO3/g-C3N4 for removal of oxytetracycline. *Catalysts*, 10(3): 301.

Yang, M., Xu, A., Du, H., Sun, C., Li, C., 2007. Removal of salicylic acid on perovskite-type oxide LaFeO3 catalyst in catalytic wet air oxidation process. *Journal of Hazardous Materials*, 139(1): 86-92.