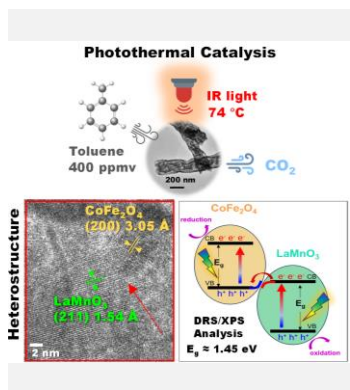


Electrospun $\text{CoFe}_2\text{O}_4/\text{LaMnO}_3$ Nano-Heterostructures for Low-Temperature Photothermal Catalytic Degradation of Toluene

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Ph.D. Student: Y
Journal: CEJ 15.1

A. Bankole¹, K. Ahmed¹, M. Abu Hajja¹, K. Polychronopoulou², M. Abi Jaoude¹. (1) Department of Chemistry, Khalifa University of Science and Technology, Abu Dhabi, UAE, 100061905@ku.ac.ae. (2) Department of Mechanical and Nuclear Engineering, Khalifa University of Science and Technology, Abu Dhabi, UAE



Perovskite oxides such as LaMnO_3 have valuable photothermal conversion capacity that is conducive to designing advanced photothermal oxidation catalysts. Nanoscale morphology engineering and heterojunction coupling of LaMnO_3 with a suitable semiconductor co-catalyst is an effective strategy to harness light and heat effects for designing low-temperature oxidative catalysis. In this study, direct Z-scheme $\text{CoFe}_2\text{O}_4/\text{LaMnO}_3$ nanocomposite fibers were prepared by electrospinning and extensively characterized. The composites were used in the continuous flow photothermal catalytic abatement of 400 ppmv toluene vapors (WHSV: $37,500 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) under infrared (IR) light irradiation, demonstrating up to 94% pollutant removal at low temperature (74 °C), with up to 92% CO_2 yield. The photothermal catalytic removal efficiency was found to be two-fold higher than that observed with thermal catalysis (in the absence of IR irradiation).

Introduction

The escalation of atmospheric environmental challenges is partly attributed to air quality degradation and the ensuing health risks posed by chronic human exposure to volatile organic compound (VOC) pollution [1]. At present, oxidative catalysis (200-500 °C) stands out as a prominent abatement technology for highly concentrated VOC streams (few thousands of mg/m^3) [1]. Alternatively, semiconductor photocatalysis offers less energy-intensive solutions for mitigating medium to low-level atmospheric VOC pollution in poorly ventilated settings [1]. However, intrinsic limitations of traditional semiconductor photocatalysts, including poor photoabsorption (i.e. fast charge carriers recombination) and poor activation by cost-efficient radiation (e.g. solar/visible and IR) underscore the need for continuously developing advanced oxidation processes and technologies [2].

Photothermal catalysis amalgamates the advantages of both thermal- and photocatalysis, garnering substantial research attention over the last ten years. Plasmon coupling of semiconductor photocatalysts with noble metal nanoparticles has been commonly used to drive photothermal catalysis [2]. However, the high cost and thermal sintering of noble metals have led to the exploration of alternative materials. Polymetallic oxides such as perovskite oxides have emerged for their remarkable light absorption capabilities, photothermal properties, and thermal stability [3]. Nevertheless, their catalytic oxidation efficiency toward VOCs is limited by their large particle size and low surface area of contact, requiring both morphological and structural engineering. One-dimensional (1D) particle geometries (e.g., nanofibers) may exhibit peculiar properties between those of isolated atoms and bulk materials. Such include a large surface area per unit mass, confinement of electronic states due

to particle size reduction, and enhanced surface selectivity owing to symmetry breaking at the boundaries [4]. Altogether, these attributes are highly interesting for improving the properties of conventional-scale heterogeneous photo- and thermal catalysts in flow-through applications where mass, charge, and heat transfer are crucial performance players. In this study, heterojunction-coupled spinel ferrite and perovskite ($\text{CoFe}_2\text{O}_4/\text{LaMnO}_3$) composite nanofibers are developed by a novel one-pot electrospinning process and studied toward the low-temperature catalytic and IR-assisted photothermal catalytic degradation of toluene in continuous flow operation.

Material and Methods

The $\text{CoFe}_2\text{O}_4/\text{LaMnO}_3$ composite heterostructure was synthesized via a one-pot electrospinning method (invention disclosure), followed by air-calcination treatment at 700 °C. Control materials of CoFe_2O_4 and LaMnO_3 were also prepared under the same reaction conditions. The materials were characterized by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX), liquid nitrogen porosimetry, transmission electron microscopy (TEM) coupled with selected-area electron diffraction (SAED), powder X-ray diffraction (p-XRD), UV-vis diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS core and valence states) to examine the microscopic morphology, microstructure, optical absorption properties, surface chemical states, and band-edge alignments, respectively. Toluene, a representative aromatic VOC, was used to investigate the adsorption behavior and degradation extent over the photothermal catalysts. Thermal and photothermal catalytic studies were conducted at 74 °C in a continuous flow reactor using an IR light source (280

mW/cm²). Each catalytic activity test involved the use of 40 mg of catalyst for the degradation of 400 ppmv toluene (WHSV: 37,500 mL·g⁻¹·h⁻¹), generated by bubbling zero air into liquid toluene. Exposure of the heterostructured nanofibers to IR radiation in the absence of other extrinsic heat sources led to an increase in the surface temperature of the catalyst to 69 °C. Therefore, all catalytic and photothermal catalytic studies were conducted at an equilibrium temperature of 74 °C for comparison purposes. The degradation efficiency was analyzed by GC-FID, while the CO₂ yield was determined by microGC-TCD measurements of sample fractions collected during both dark and light irradiation conditions for two hours after thermal equilibrium. Additionally, GC-MS was performed to identify potential degradation byproducts and stable intermediates.

Results and Discussion

Our findings demonstrate the presence of preserved spinel ferrites (CoFe₂O₄) and lanthanum manganite (LaMnO₃) phase structures within the hollow-core composite nanofibers, as confirmed by p-XRD patterns (Figure 1). TEM measurements confirmed these findings and evidenced the existence of heterojunctions in the CoFe₂O₄/LaMnO₃ nanofibers.

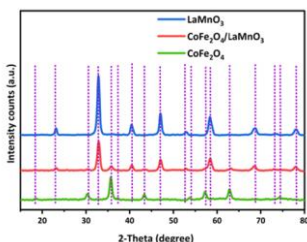


Figure 1 p-XRD patterns of CoFe₂O₄/LaMnO₃ composite fibers and respective single-system fibers

The composite nanofibers exhibited a mesoporous texture with a surface area of 26 m²/g, and average pore size of 25 nm. XPS analysis demonstrated the presence of adsorbed surface oxygen species, which indicated the presence of oxygen vacancies. DRS analysis coupled with XPS valence state

Conclusions

Z-scheme heterostructured mixed metal-ferrite/perovskite oxide (CoFe₂O₄/LaMnO₃) nanofibers were developed by one-pot electrospinning. The mixed system demonstrated superior photothermal catalytic mineralization of toluene at near ambient temperature, under IR irradiation, compared to thermal catalysis.

Acknowledgments

This work was financially supported by Khalifa University (KU) through the Center for Catalysis and Separation (CeCaS).

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measurements enabled the hypothesis of a direct Z-scheme heterojunction between the two oxides [5], with segregated charges, and an electron-hole pair recombination path across the conduction band (CB) of LaMnO₃ and the valence band (VB) of CoFe₂O₄. Following the establishment of optimum adsorption-desorption equilibrium, photothermal catalysis at 74 °C exhibited enhanced degradation of toluene (~82-94%, Figure 2a) compared to thermal catalysis (~29-61%, Figure 2b) at the same temperature. The CO₂ yield resulting from the photothermal catalytic process reached ~79-92% during two hours.

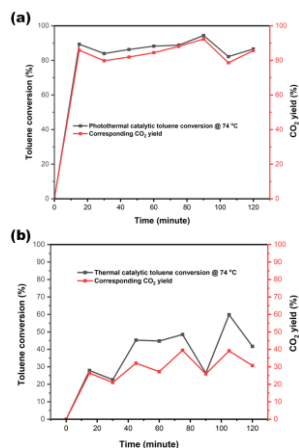


Figure 2 (a) Photothermal catalytic and CO₂ yield (b) Thermal catalytic and CO₂ yield (toluene:400 ppmv, WHSV: 37500 mL·g⁻¹·h⁻¹, catalyst weight: 40 mg, zero air gas flow rate: 25 mL/min; IR light irradiance: 280 mW/cm²).

The observed high toluene removal efficiencies with CoFe₂O₄/LaMnO₃ compared with the control single oxide fibers can be attributed to its larger average crystallite size, reaching up to 159 nm (p-XRD). Furthermore, the mixed CoFe₂O₄/LaMnO₃ system impeded the formation of stable toluene intermediates, as confirmed by qualitative GC-MS analysis, indicating superior performance. Understanding the mechanistic insights of toluene degradation and the analysis of the direct Z-scheme charge transfer flow path are underway.