Removal of nitric oxide by perovskite LaFeO₃-LaMnO₃ composite nanoarray

Guan-Ting Pan,^a Chih-Wen Huang,^a Thomas C.-K. Yang,^{a,*} Siewhui Chong^b

^aDepartment of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei City 106, Taiwan (R.O.C.) ^bDepartment of Chemical and Environmental Engineering, University of Nottingham, Semenyih, Selangor 43500, Malaysia

*Corresponding author: +886-2-27760985, ckyang@ntut.edu.tw

Abstract: Nitric oxide (NO) is one of the major air pollutants causing critical environmental and human health issues. Doping of transition metal on lanthanum perovskite catalyst has shown effectiveness in removing this air pollutant. The aim of this study is to prepare and evaluate one-dimensional ordered lanthanum iron oxide-lanthanum manganese oxide (LaFeO₃-LaMnO₃) composite nanoarrays using sol-gel method, with anodized aluminum oxide (AAO) as the array template. LaMO₃ and LaFeO₃ phases were identified with XRD; and the samples were found to be nanorod arrays of 15 μ m long with diameters ranging from 0.5 to 1.0 μ m. DRIFTs was used to evaluate the NO removal efficiency at different temperatures. The best sample was LaFeO₃-LaMnO₃ nanoarrays with La(NO₃)₃: Mn(NO₃)₂: Fe(NO₃)₃: C₆H₈O₇ volume ratio of 5: 2: 3: 10, which yielded 65% NO conversion at 200°C.

Keywords: Nitrous oxide, Nanoarray, Perovskite.

1. Introduction

Nitrous oxides (NOx) are one of the main hazardous sources and are poisonous not only to human health [1], but also one of the main culprits causing acid rain, photochemical smog, ozone depletion, and particulate matter [2]. In our previous study [3], 1D ordered zinc: copper indium sulfide has shown good performance in the photosynthesis of methanol. A number of studies have also shown that one-dimensional ordered nanostructure can significantly enhance the conversion rates due to the noticeable improvement of charge transfer. Therefore, this study aims to explore the feasibility of 1D ordered lanthanum iron oxide-lanthanum manganese oxide (LaFeO₃-LaMnO₃) composite nanoarrays for removal of nitric oxide (NO).

2. Experimental

The 1D ordered LaFeO₃-LaMnO₃ composite nanoarrays were prepared from the solutions of 5 M lanthanum (III) nitrate (La(NO₃)₃), 5 M manganese (II) nitrate (Mn(NO₃)₂), 5 M iron (III) nitrate (Fe(NO₃)₃· 9H₂O) and 1 M citric acid (C₆H₈O₇),. Anodized aluminum oxide (AAO) templates were soaked in the solutions for 10 min at 25°C. After the growth of nanoarrays in the AAO templates, the aluminum frameworks were etched by sodium hydroxide solution. Samples (a)–(f) as labelled in Table 1 were synthesized by soaking the AAO templates with different LaFeO₃-LaMnO₃ mixture solutions. The films were then dried in oven at 110°C for 1 h, followed by heat treatment in a furnace under argon/hydrogen gas at 650°C for 4 h. This annealing treatment is necessary as it provides better and stable crystal properties. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) was used to evaluate the efficiencies of NO removal at different temperatures with an initial NO concentration of 3,000 ppm, and a flow rate of 5 sccm. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and photoluminescence (PL) characterization tests were carried out to evaluate the properties of the samples.

Reagent/Sample	(a)	(b)	(c)	(d)	(e)	(f)
5M La(NO ₃) ₃ /mL	5	5	5	5	5	5
$5M Mn(NO_3)_2/mL$	5	4	3	2	1	
5M Fe(NO ₃) ₃ • 9H ₂ O /mL	-	1	2	3	4	5
$1M C_6H_8O_7/mL$	10	10	10	10	10	10

Table 1. The parameters of various samples prepared using sol-gel method.

3. Results and discussion

Figure 1 shows the XRD patterns of different 1D ordered LaFeO₃-LaMnO₃ composite nanoarrays. The diffraction peaks of all samples were indexed to the standard cards of LaMO₃ (JCPDS NO. 01-075-0440) and LaFeO₃ (JCPDS NO. 01-075-0541). In addition, a shift of the main peak to a higher 2θ angle was observed in samples with the increasing Fe concentrations, due to an intrinsic defect of the LaFeO₃-LaMnO₃ composite nanoarrays crystal structure. According to the FESEM micrographs in Figure 2, nanorod arrays were 15 µm long with diameters ranging from 0.5 to 1.0 µm. Figure 3 shows the removal efficiencies of NO by 1D ordered LaFeO₃-LaMnO₃ composite nanoarrays. Apparently, higher temperatures favor NO removal. Sample (d) was found to be the best sample, yielding NO removal efficiency of 65% at 200°C. As supported by the PL result (not shown), sample (d) shows a lower photoluminescence intensity, indicating lower recombination rate of photo-generated electron charges and thus higher activity.



Figure 3. NO removal efficiencies of different LaFeO3-LaMnO3 samples.

4. Conclusions

1D ordered LaFeO₃-LaMnO₃ composite nanoarrays were successfully prepared using sol-gel method with AAO templates. XRD showed that the LaMO₃ and LaFeO₃ phases were the major crystal structures. NO removal efficiency increases with the operating temperature. Highest NO conversion of 65% was achieved by LaFeO₃-LaMnO₃ nanoarray with La(NO₃)₃: Mn(NO₃)₂: Fe(NO₃)₃: C₆H₈O₇ volume ratio of 5: 2: 3: 10. In conclusion, LaFeO₃-LaMnO₃ composite nanoarray has shown its potential in removing NOx.

References

- 1. Elser, M., et al., *New insights into PM 2.5 chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry*. Atmospheric Chemistry and Physics, 2016. **16**(5): p. 3207-3225.
- 2. Yu, J., et al., *Sulfur poisoning resistant mesoporous Mn-base catalyst for low-temperature SCR of NO with NH 3*. Applied Catalysis B: Environmental, 2010. **95**(1): p. 160-168.
- 3. Yang, S.-W., et al., *The photosynthesis of methanol on 1D ordered Zn: CuInS 2 nanoarrays*. Journal of the Taiwan Institute of Chemical Engineers, 2014. **45**(4): p. 1509-1515.