3D perovskite/metal oxide composite nanorod array based monolithic catalysts for automotive emission control

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Introduction

Metal oxides are considered to be an important component in many catalysts that are being used in modern chemical industry.[1] Among the mixed metal oxides, perovskite-type oxides have attracted attention for automobile exhaust removal, clean and renewable energy due to their interesting catalytic functions.[1][2] The influence of B sites of $LaMeO_3$ perovskite on physicochemical properties and catalytic performance has been studied, suggesting $LaCoO_3$ exhibited better catalytic performance for NO oxidation than $LaFeO_3$ and $LaMnO_3$ [3] Jian et al. reported ZnO/(La, Sr)CoO_3 core-shell composite nanorod array on 2D substrate prepared using a two-step method, which exhibited better photocatalytic properties than homogeneous ZnO nanorod arrays and LSCO film alone.[2] Recently, by using low temperature solution based method, monolithic integration of nanowires onto commercial cordierite honeycombs has been achieved in our lab, giving rise to a new type of structured catalysts with ultra-efficient materials utilization, excellent robustness, tunable and good catalytic performance.[4][5] Herein, we report a cost-effective and generic preparation method to further integrate the 3D metal oxide nano-array catalysts with perovskite-type $LaMeO_3$(Me=Fe, Co, Mn, Ni , Cu) nanoparticle films, which has further tuned the nano-array catalysts' catalytic performance toward automotive emission control, such as the oxidation of CO, NO, and HCs.

Materials and Methods

The ZnO nanorod arrays were grown upon the monolithic honeycomb cordierite through hydrothermal method. Desired length to diameter ratio of nanorods could be achieved by tuning different parameters such as the concentration of solution, growing temperature as well as growing time.[4][5] For $LaMeO_3$ film, different colloidal solutions were prepared using nitrate salts as the precursors and ethoxyethanol as solvent. Certain amount of polyvinylpyrrolidone was added into the solution to increase the viscosity. Then using a simple dip coating method, a coating could be achieved on 3D monolithic cordierite. Finally, the substrate was annealed at 300°C for 30 minutes and 800°C for an hour.
The low temperature oxidations of CO, NO and hydrocarbon were investigated by using BenchCAT reactor connected to micro-GC, or FT-IR spectrometer. The space velocity of all the catalyst tests was controlled to be ~45,000/h and about 0.1g monolithic catalyst was used.

Results and Discussion

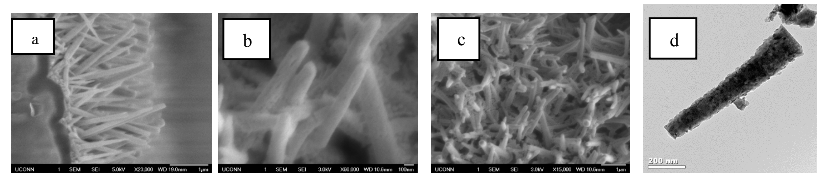
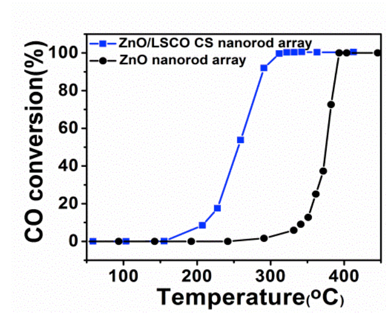


Figure 1 (a) A SEM image for cross section of ZnO nanorods arrays on 3D honeycomb cordierite. **(b,c)** side view and top view SEM images of $LaMnO_3$/ZnO composite nanorod arrays using dip coating method. **(d)** A TEM image of an individual $LaMnO_3$/ZnO composite nanorod.



Compared to 3D ZnO nanorod array monolith, ZnO/LSCO composite nanorod array catalyst lowers the light-off temperature of CO oxidation from 380°C to 260°C. The large specific surface area of ZnO nanorod array enhanced the effective dispersion of perovskite nanoparticle catalysts, therefore interaction with the gas flow. The NO oxidation and CO oxidation of other $LaMeO_3$/ZnO composite nanorod array catalyst are also comparatively studied.

Figure 2 CO conversion versus temperature of ZnO/$LaSrCoO_3$ nanorod arrays

Significance

Integration of perovskite nanoparticles with ZnO nanorods array rooted 3D monolithic honeycombs presents a new type of structured catalysts for automotive emission control. The perovskite nanoparticle films add up new catalytic functions such as oxygen storage capacity toward enhanced molecular oxidation to the new class of nano-array based structured catalysts with high materials utilization efficiency, excellent robustness, and functional tunability.

References

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