

## Supporting Information

Ce- and Mn-enhanced perovskite catalyst with exsolved Ni particles for H<sub>2</sub> production from CH<sub>4</sub> reforming

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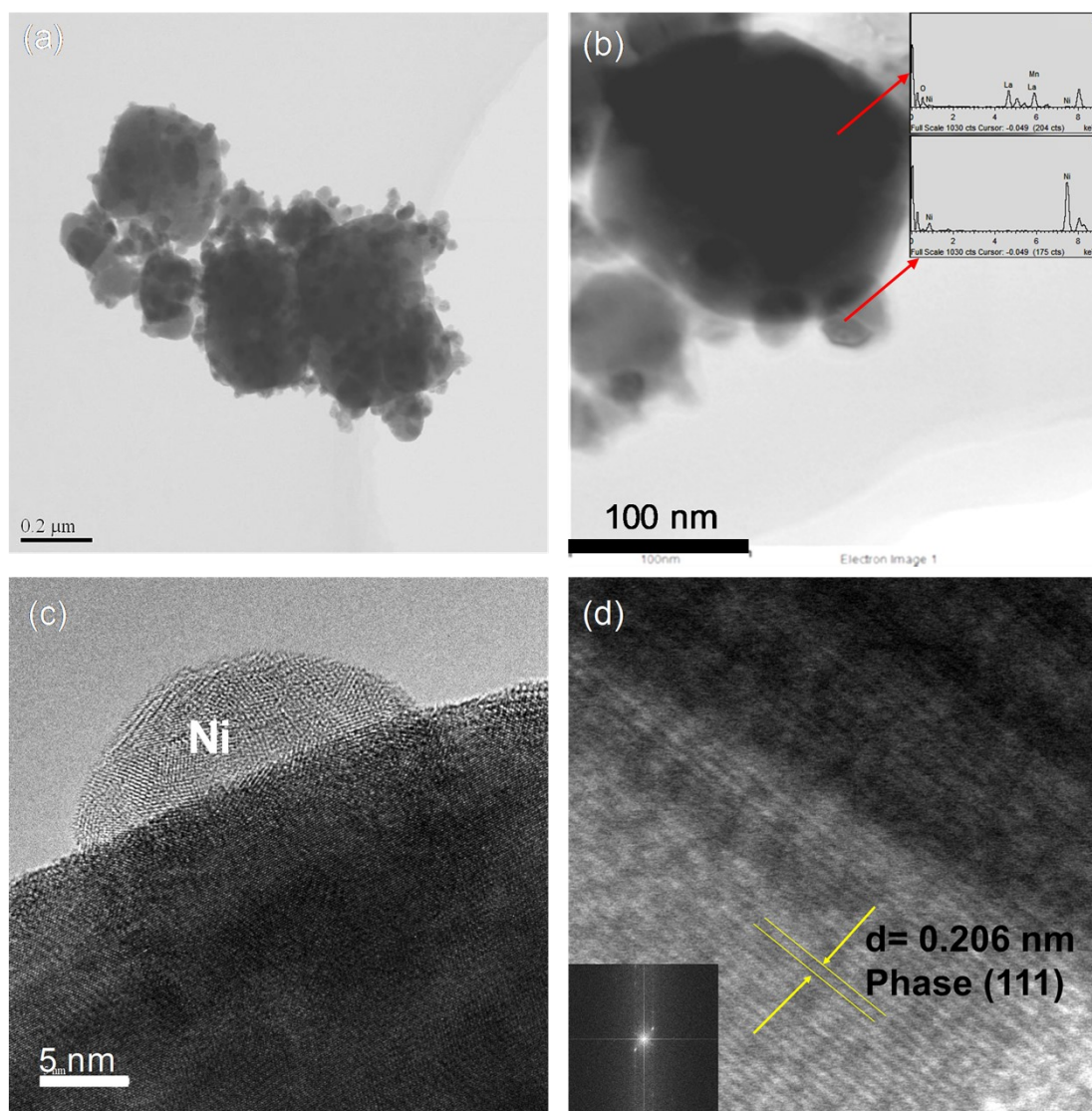


Fig. S1. Bright field TEM images of in situ exsolved Ni nanoparticles in reduced-LCMN-05: (a) Low magnification of the exsolved Ni nanoparticle on the surface of the substrate; (b) EDX composition analysis; (c) high magnification of the exsolved Ni nanoparticle; (d) lattice fringe of exsolved Ni particle.

The EDX composition analysis and lattice fringe confirmed the exsolution of metallic Ni particles with average size of 15 nm in reduced LCMN-05.

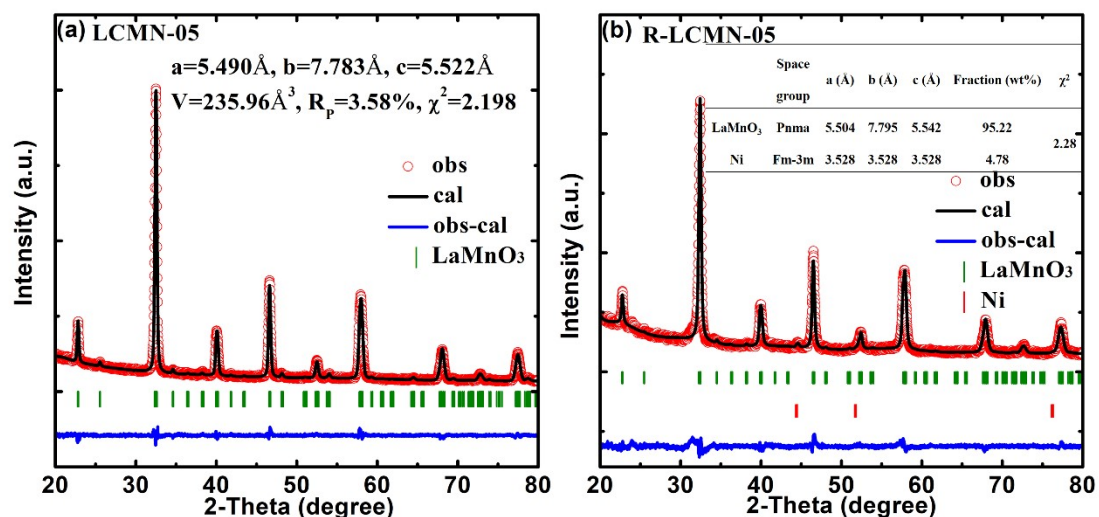


Fig. S2. Rietveld refinement of the room temperature powder XRD pattern using Pnma space group for LCMN-05 (a) and R-LCMN-05 (b).

The obtained diffraction data was refined by the Rietveld method using EXPGUL [1, 2] software to determine the crystal structure and lattice parameters. During refinements, the scale factor, zero shift, background parameters, peak profile parameters, lattice parameters, atomic position and thermal factor were optimized.

For R-LCMN-05, the perovskite phase was refined with Pnma space group model and the metallic Ni phase with Fm-3m space group. The weight ratio of Ni and perovskite could be calculated by GSAS software after the confidence factor was optimized.

The amount of metallic Ni was 4.78wt% indicating 80% (0.16mol%) of Ni element were exsolved from the bulk onto the surface approximately.

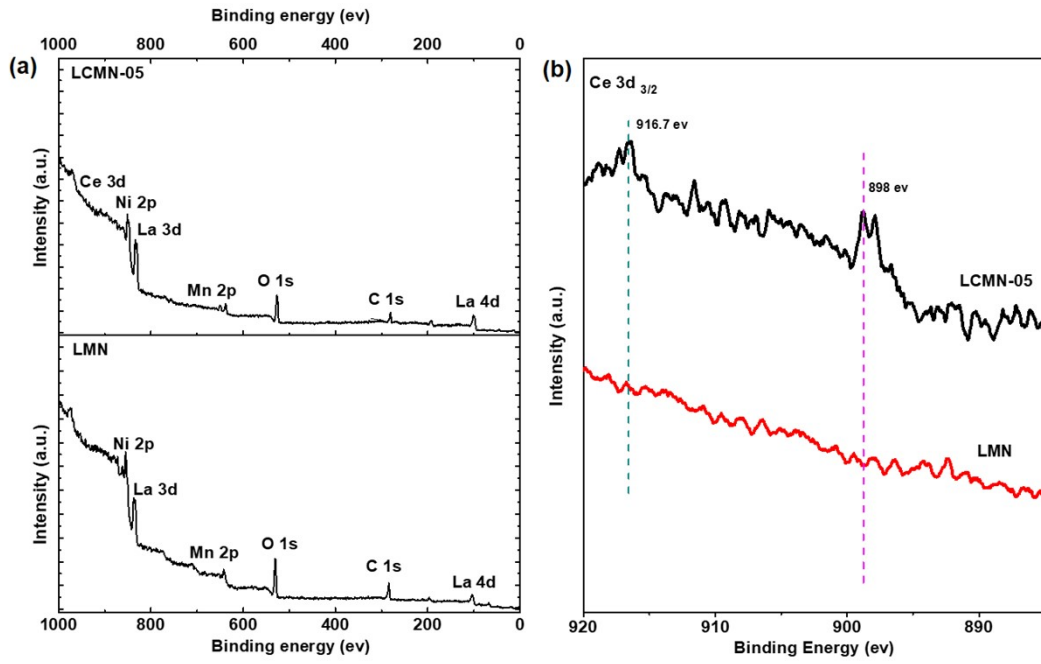


Fig. S3. Representative XPS and Ce-XPS spectra of LMN and LCMN-05.

Ce 3d core-level spectra was detected in the XPS profiles of LCMN-05, showing a successful doping of Ce.

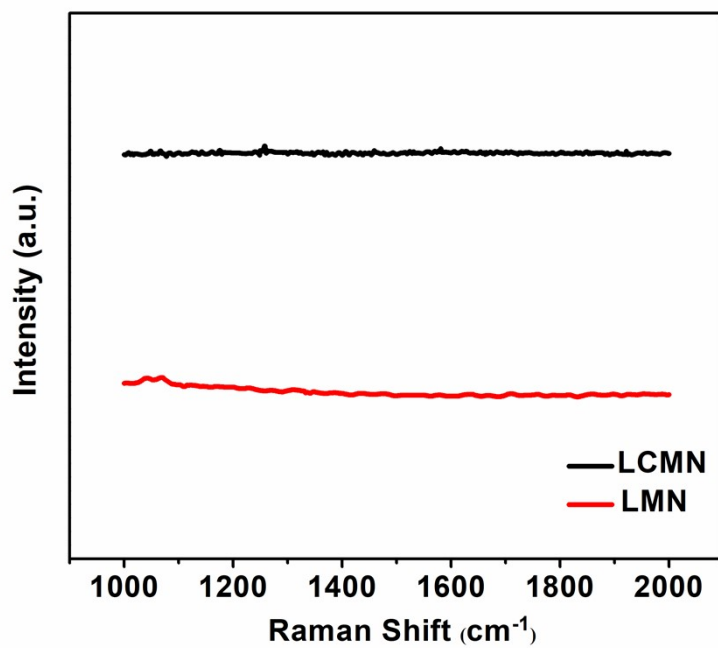


Fig. S4. Raman spectra of the fresh R-LMN and R-LCMN-05, showing no characteristic peak for the fresh reduced catalyst before the reforming test.

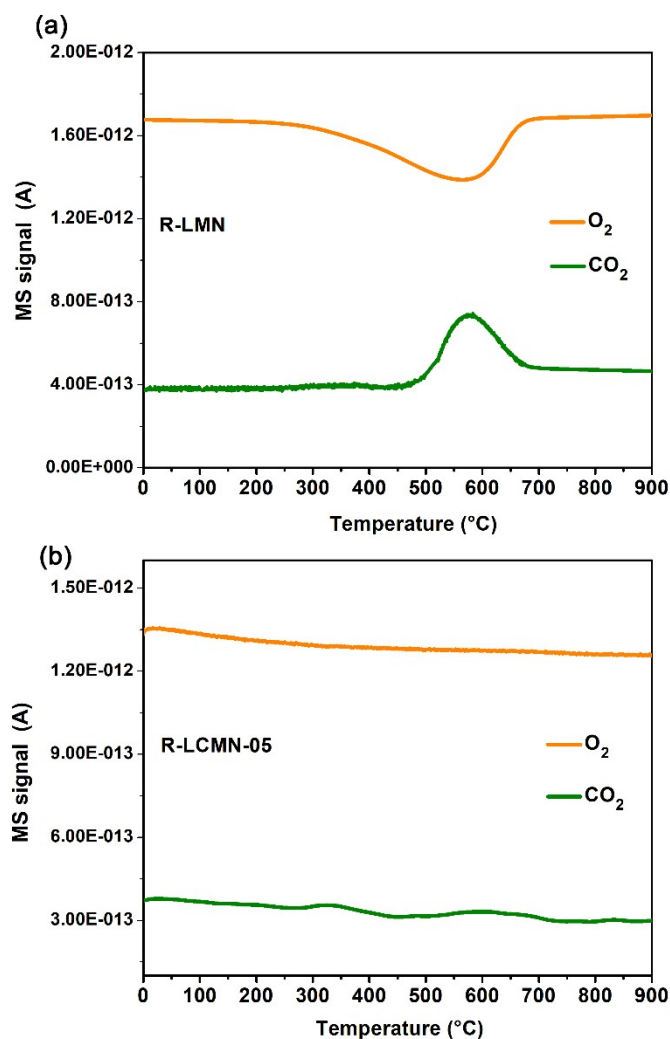


Fig. S5. O<sub>2</sub> and CO<sub>2</sub> signals during the temperature programmed oxidation tests for the R-LMN (a) and R-LCMN-05 (b) after test.

R-LMN catalyst showed a typical CO<sub>2</sub> release peaks centered at 600 °C. The peak at the high temperature was assigned to relatively inert carbon species which can react with O<sub>2</sub> to form CO<sub>2</sub>. The O<sub>2</sub>-TPO results also indicated the formation of large amounts of coke on the R-LMN catalyst while no CO<sub>2</sub> release peaks was detected for R-LCMN-

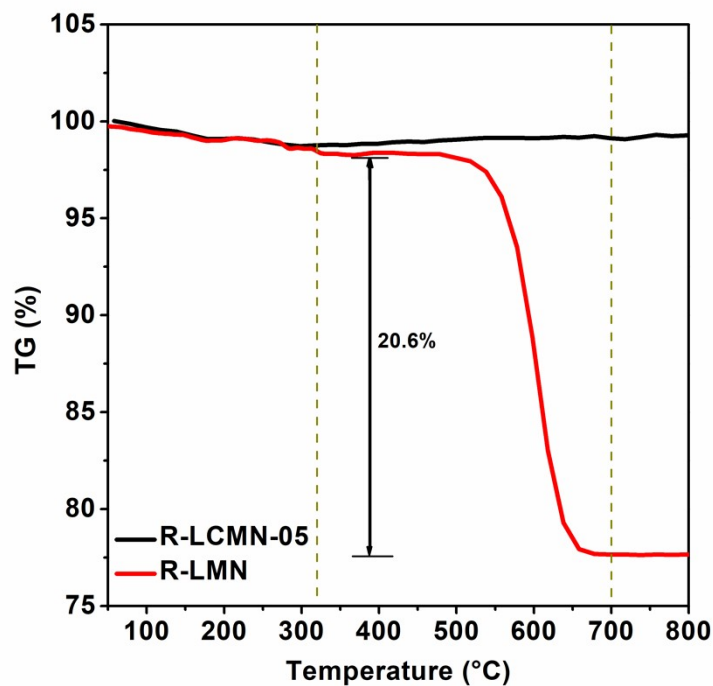


Fig. S6. TGA profiles of post-test catalysts (R-LMN and R-LCMN-05).

The thermogravimetric analysis was conducted for the post-test catalyst in air condition from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> to identify and determine the amount of deposited carbon.

As shown in Fig. S4, the weight loss below 300°C was ascribed to the water evaporation, and over 700 °C, the weight loss was negligible. Thus, the amount of coke on the catalyst surface was calculated based on the weight loss between 300 and 700°C. The results showed the tested R-LMN had a weight loss of 20.6%, while the weight had a slightly increase above 300°C for test R-LCMN-05, which was due to the oxidation of the exsolved metallic Ni and the perovskite. Thus, it can be concluded that there was barely any carbon deposition in the R-LCMN-05 while amount of coking in R-LMN.

Reference:

- [1] B. H. Toby, *Journal of Applied Crystallography* 2001, 34, 210.
- [2] R. B. Von Dreele, A. C. Larson, *Los Alamos National Laboratory Report LAUR* 1994, 86-748.