## Supplementary Information

## Facile Synthesis of Hollow Hierarchical Ni/γ-Al<sub>2</sub>O<sub>3</sub> Nanocomposites for Methane Dry Reforming Catalysis

Qing Zhang<sup>1</sup>, Tao Wu<sup>1</sup>, Peng Zhang<sup>1</sup>\*, Ruijuan Qi<sup>2</sup>, Rong Huang<sup>2</sup>, Xuefeng Song<sup>1</sup>, and Lian Gao<sup>1</sup>\*

1. State Key Lab of Metal Matrix Composites

School of Materials Science and Engineering

Shanghai Jiao Tong University

800 Dongchuan Rd.

Shanghai, P. R. China 200240

2. Key Laboratory of Polar Materials and Devices

Ministry of Education

East China Normal University, Shanghai, China

\*E-mail address: liangao@mail.sic.ac.cn (L. Gao); pengzhang2010@sjtu.edu.cn

(P. Zhang)

Tel: +86-12-52412718. Fax: +86-21-52413122

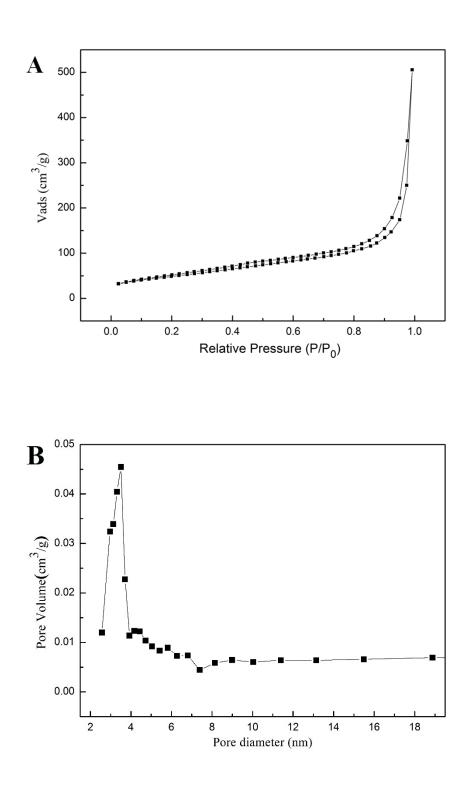
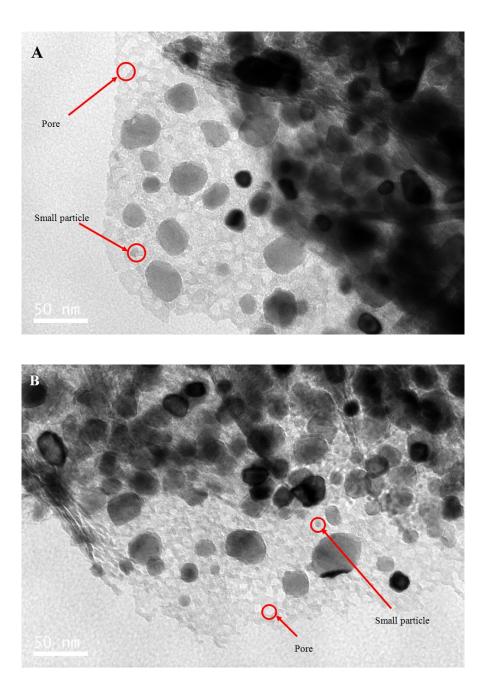
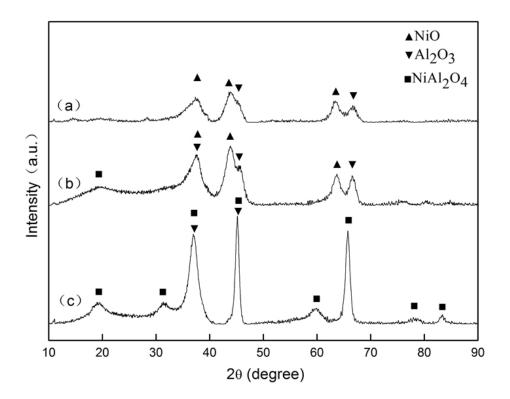


Figure S1. (A)  $N_2$  adsorption and desorption data and (B) corresponding pore size distribution of the hierarchical hollow Ni/Al<sub>2</sub>O<sub>3</sub> (NAO, 35 wt%).



**Figure S2**. The morphology of hierarchical hollow Ni/Al<sub>2</sub>O<sub>3</sub> (NAO, 35 wt%) annealed at (A) 400  $^{\circ}$ C and (B) 600  $^{\circ}$ C after H<sub>2</sub> reduction at 700  $^{\circ}$ C for 2 h.



**Figure S3**. XRD patterns of hierarchical Ni/Al<sub>2</sub>O<sub>3</sub> composite calcined at various temperatures (a) 400 °C, (b) 600 °C and (c) 800 °C.

**Table S1.** The XPS information NOAO samples with various Ni loadings and different calcination temperatures.

Catalyst	Binding Energy (eV)			NI:/A1	Ni loading	Theoretical Ni
	Ni 2p <sub>3/2</sub>	Al 2p	O 1s	Ni/Al	(%)	loading (%)
400 °C	855.1	73.1	531.6	0.219	25.2	
600 °C	855.2	74.3	531.1	0.233	26.9	35.3
800 °C	857.0	73.8	529.8	0.226	26.0	
800 °C	856.8	74.4	531.0	0.250	38.9	47.0
600 °C	856.8	73.9	531.1	0.486	56.0	57.7

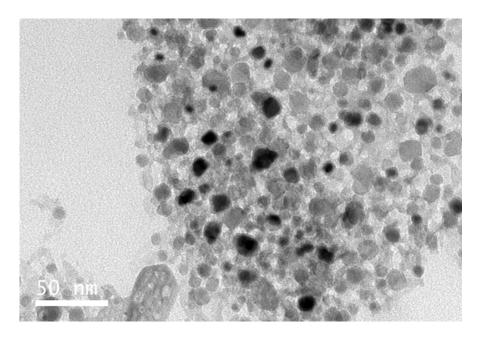


Figure S4. The TEM image of NAO (58 wt%, 800 °C) after long-term test.

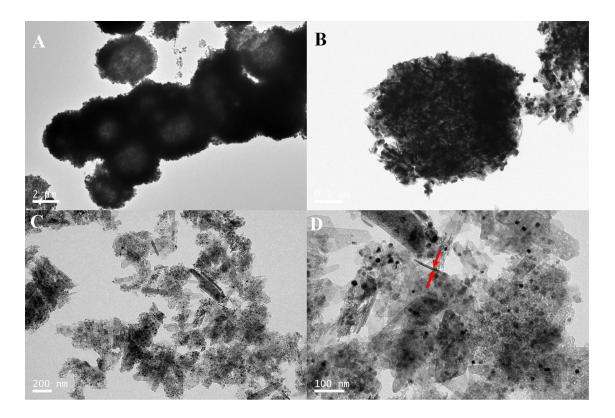
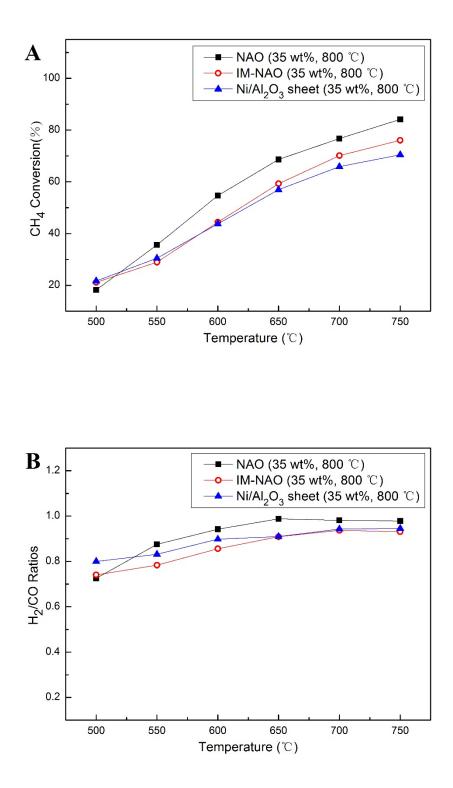
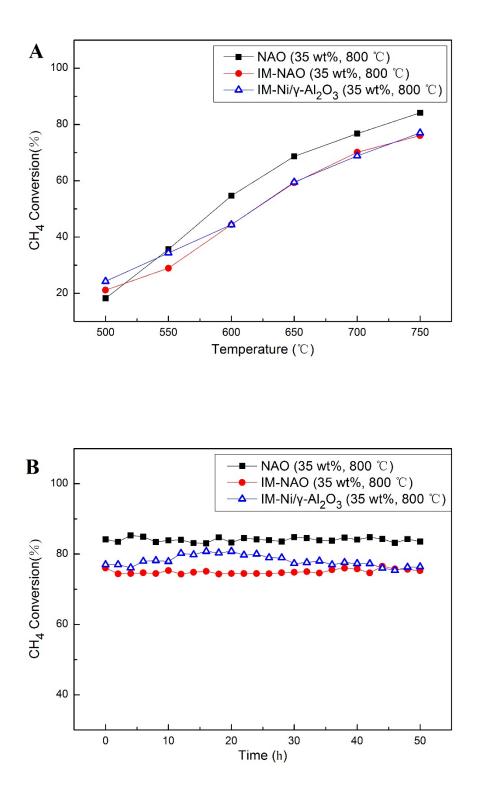


Figure S5. The morphologies of the IM-NAO (A, B) and Ni/Al<sub>2</sub>O<sub>3</sub> nanosheet (C, D) after  $H_2$  reduction at 700 °C for 2 h.



**Figure S6**. (A) Methane conversion and (B) H<sub>2</sub>/CO ratio of the DRM catalysis products for sample NAO (35w%, 800 °C), IM NAO (35w%, 800 °C), and Ni/Al<sub>2</sub>O<sub>3</sub> sheet (35w%, 800 °C).



**Figure S7**. (A) Methane conversion of DRM catalysis at different temperatures, (B) Methane conversion of DRM catalysis in a long term test (50 h) at 750 °C for sample NAO (35w%), IM NAO (35w%), and IM-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (35w%).

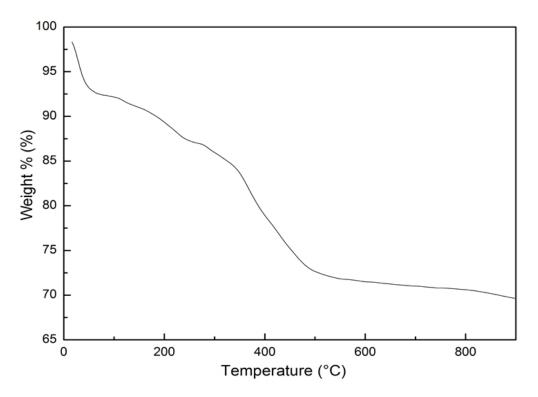


Figure S8. The TG analysis of NiAl-LDH precursor.

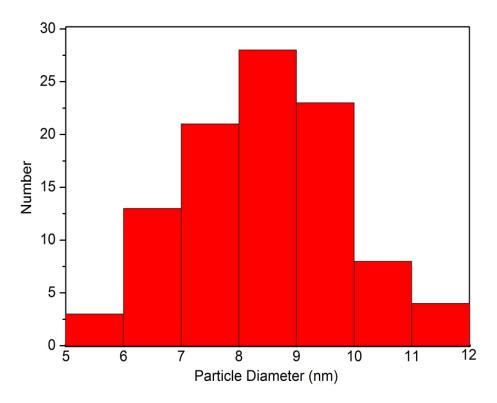


Figure S9. The particle distribution of NAO (35 wt%, 800 °C) after long-term test.

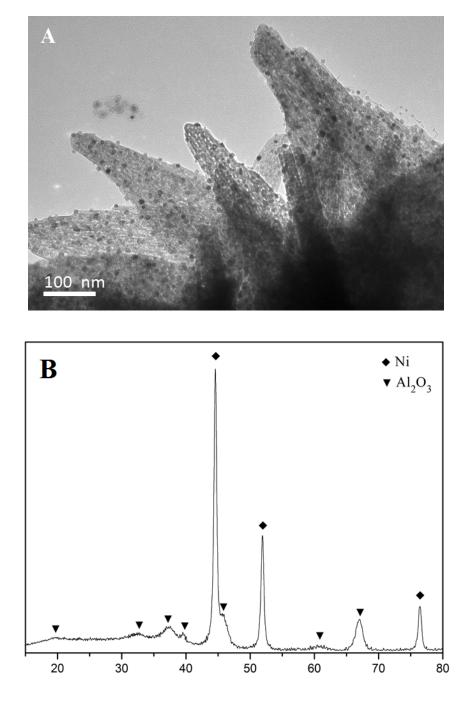


Figure S10. The TEM image and XRD pattern of NAO (35 wt%, 800 °C) after long-term test.