Supporting Information

La$_2$O$_3$ catalysts with diversely spatial dimensionality for oxidative coupling of methane to produce ethylene and ethane

Tao Jiang,$^{a,b}$ Jianjun Song,$^{a,b}$ Minfeng Huo,$^{a,c}$ NaTing Yang,$^{a,b}$ Jingwei Liu,$^a$ Jun Zhang,$^a$ Yuhan Sun*$^a$ and Yan Zhu*$^{a,c}$

$^a$ CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

$b$ University of Chinese Academy of Sciences, Beijing 100049, China

$c$ School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

Experimental:

Synthesis of La$_2$O$_3$ nanoparticles: 3.5 g C$_7$H$_5$O$_4$N was added in a 50 mL solvent mixed with 80% alcohol and 20% deionized water. Then 5 mL 0.5 M La(NO$_3$)$_3$ was dropped into the above solution, and stirred for about 1 hour. After that, the mixture was putted to the 100 mL autoclave and then kept at 120°C for 24 hours. After the claves cooled to room temperature, the product was separated and washed by centrifugation by alcohol and deionized water. Finally the product was dried at 80°C and calcined at 680°C for 3 hours.

Synthesis of La$_2$O$_3$ nanorods: 4.33 g La(NO$_3$)$_3$.6H$_2$O and 2.22 g PVP(10000) were added to 200 mL deionized water, and stirred for about 2 hours. Then the ammonia was added to the solution slowly and the solution became white. The gel sample was transferred to 100 mL autoclave and heated at 150°C for 24 hours. The product was separated and washed by deionized water after the autoclaves cooled down. Finally the product was dried at 80°C in a drying cabinet and calcined for 3 hours at 680°C at furnace.

Synthesis of La$_2$O$_3$ nanosheets: 1.625 g La(NO$_3$)$_3$.6H$_2$O and 6 mL PEG400 were added in 50 mL deionized water, and stirred for 3h at 40°C. After that, the solution
was transferred to 100 mL autoclave and heated at 150°C for 24 hours. The product was washed with deionized water. Finally the product was dried at 80°C in a drying cabinet and calcined for 2 hours at 680°C at furnace.

**Synthesis of La$_2$O$_3$ nanoflowers:** 10 g La(NO$_3$)$_3$·6H$_2$O, 2 mL water and 2 mL acetic acid were mixed into 60 mL glycol, then and stirred them for about 3 hours until dissolved. The solution was transferred into 100 mL autoclave and heated at 180°C for 3 hours. After the autoclaves cooled down, the product was separated and washed for 5 times in alcohol. The product was dried at 80°C and calcined for 2 hours at 680°C.

**OCM catalytic test**
The oxidative coupling of methane (OCM) activity was evaluated in fixed bed quartz tubular reactor in at atmospheric pressure. 0.2 g 40-60 mesh La$_2$O$_3$ catalyst and 0.8 g silica sand were mixed together and then putted in quartz tubular. The catalyst was pretreated in N$_2$ atmosphere with 30 mL/min flow rate at 800°C for 2 hours. When the feed temperature dropped to 400°C, the reactant gas was went into fixed bed reactor in the rate of 240 mL/min which consist of 75% methane and 25% oxygen. A cold trap was placed at the outlet of the quartz tube to separate any condensed water vapor from the reaction products. And the products were detected online by a micro gas chromatograph (3000 Micro GC; Inficon) equipped with two thermal conductivity detectors (TCD), one Molecular sieve 5A and one Plot U columns.

**Characterization**
SEM characterization was detected by ZEISS Supra 55. Powder XRD measurements were carried out with a Rigaku D/Max-RB X-ray diffractometer with Cu Kα radiation. TEM characterization was performed with JEOL JEM-2100 Electron Microscope (JEOL). The Brunauer–Emmett–Teller (BET) surface areas were recorded by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). X-ray photoelectron spectra (XPS) were detected on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. CO$_2$ temperature-programmed desorption measurements were examined on Micromeritics AutoChem II 2920 instrument connected to a MKS cirrus mass spectrometer and our CO$_2$-TPD data was from mass
signal of molecular weight 44. The catalyst power (150 mg) was heated a He flow from 60 to 800°C with a heating rate of 10°C/min and then keep for 60 min at 800°C, and cooled down to 60°C. The CO₂ was injected at 60°C for 60 min. after that He was injected and flow for 60 min, finally the temperature was raised to 880°C with a rate of 10°C/min, the CO₂ desorption was detected by mass spectrograph.
Supporting Figures

**Fig.S1** XRD patterns of La$_2$O$_3$ catalysts.

**Fig.S2** (a) Feed and bed temperatures for OCM reaction over La$_2$O$_3$ catalysts. (b) Spatial temperature distribution in silica tube for OCM reaction over La$_2$O$_3$ catalysts.
Fig.S3 The catalytic results of only silica sand for OCM reaction.
(a) 

(b) 

(c)
**Fig. S4** The N\textsubscript{2} adsorption-desorption isotherms of La\textsubscript{2}O\textsubscript{3} catalysts after catalytic reaction: (a) nanoparticles, (b) nanords, (c) nanosheets, and (d) nanoflowers. Insets are corresponding pore-size distributions.

**Fig. S5** The stability of 2D La\textsubscript{2}O\textsubscript{3} and 1D La\textsubscript{2}O\textsubscript{3} catalysts for OCM reaction at 550°C.