## Supplementary information

## Carbon monoxide formation as an intermediate product in photocatalytic steam reforming of methane with lanthanum-doped sodium tantalate

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Fig. S1 Scheme of the flow reactor employed in the photocatalytic reaction test for PSRM <sup>1-3</sup>



**Fig. S2** X-ray diffraction patterns of the samples, (a) non-doped NTO, (b) NTO:La(0.5), (c) NTO:La(1), (d) NTO:La(2), (e) NTO:La(5), and (f) NTO:La(2)SS.



**Fig. S3** Relationship between particle size and BET surface area of the bare NTO and NTO:La samples prepared by a flux method. The symbols are the actual data. The dashed line was the curve expected from the values for the NTO:La samples with 0–1% of La doping.



**Fig. S4** DR UV-Vis Spectra of the samples, (a) non-doped NTO, (b) NTO:La(0.5), (c) NTO:La(1), (d) NTO:La(2), (e) NTO:La(5), and (f) NTO:La(2)SS.



**Fig. S5** Photocatalytic production rates of CO (circle), CO<sub>2</sub> (square), and H<sub>2</sub> (diamond) equipped with the CO selectivity (triangle) in various reaction conditions, (A) various flow rates of the feed gas mixture: 15, 30, and 50 ml min<sup>-1</sup>; light intensity, 35 mW cm<sup>-2</sup>; feed gas composition: CH<sub>4</sub> (35%), steam (2%), and Ar (balance); the photocatalyst, the NTO:La(2) sample, and (B) various CH<sub>4</sub>/H<sub>2</sub>O ratio in the feed gas: CH<sub>4</sub> (10–40%), steam (1.9-2.8%), and Ar(balance); light intensity, 165 mW cm<sup>-2</sup>; flow rate, 15 ml min<sup>-1</sup>; the photocatalyst, the NTO:La(1) sample. The photocatalyst used was 1.2 g and the irradiation area was 6 cm<sup>2</sup>, in common.



**Fig. S6** Photocatalytic production rates of H<sub>2</sub> (white bar), CO (black bar), CO<sub>2</sub> (gray bar) as well as  $S_{CO}$  (white triangle, the CO selectivity) in different CH<sub>4</sub> concentrations, (a) 25% of CH<sub>4</sub>, 2.4% of steam, 72.6% of Ar and (b) 90% of CH<sub>4</sub>, 0.3% of steam, 9.7% of Ar, over the NTO:La(1) photocatalyst. Photocatalyst: 1.2 g, photoirradiation area: 6 cm<sup>2</sup>, and light intensity: 165 mW cm<sup>-2</sup>. Sampling was carried out after 2 hours irradiation.

Entry	Sample	Metal loading amount (wt%)	Production rate / $\mu$ mol h <sup>-1</sup>			C (0/)	
			H₂	CO	CO2	S <sub>co</sub> (%)	R
1	NTO:La(1)	-	8.0	0.4	1.6	20%	1.1
2	Pt(0.1)/NTO:La(1)	0.1	10.2	0.0	2.7	0%	1.0
3	Pd(0.1)/NTO:La(1)	0.1	9.1	0.0	0.2	0%	12.8
4	Au(0.1)/NTO:La(1)	0.1	7.7	0.3	1.4	17%	1.2
5	Ag(0.1)/NTO:La(1)	0.1	3.6	0.1	0.3	17%	2.4
6	NiO(0.7)/NTO:La(1)	0.7	5.5	0.0	0.4	0%	3.1
7	CuO(1)/NTO:La(1)	1	3.9	0.1	0.7	16%	1.3
8	ZnO(1)/NTO:La(1)	1	0.1	0.0	0.0	0%	-
9	non-doped NTO	-	1.3	0.0	0.0	0%	-
10	Ga <sub>2</sub> O <sub>3</sub>	-	2.2	0.1	0.4	19%	1.1
11	ZnO	-	0.3	0.0	0.0	0%	-
12	TiO₂	-	0.2	0.0	0.0	0%	-

Table S1 Photocatalytic activity of various photocatalysts in the PSRM<sup>a</sup>

<sup>*a*</sup> Reaction conditions: photoirradiation area, 6 cm<sup>2</sup>; feed gas: 25% CH<sub>4</sub>, 72.6% Ar, and 2.4% steam (total flow rate: 15 ml min<sup>-1</sup>); light intensity: 27 mW cm<sup>-2</sup>.

## References

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- 3 A. Anzai, K. Fujiwara, A. Yamamoto and H. Yoshida, *Catal. Today*, 2020, **352**, 1–9.