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Supporting Information

Light Assisted CO₂ Reduction with Methane over SiO₂ Encapsulated Ni Nanocatalysts for Boosted Activity and Stability

Huimin Liu, Xianguang Meng, Thang Duy Dao, Lequan Liu, Peng Li, Guixia Zhao, Tadaaki Nagao, Liuqing

Yang, and Jinhua Ye*

Table S1 Assumed wavelength center of the introduced light, calculated photon numbers and activity

Filters	Light intensity	Assumed wavelength	Number of	CO ₂ conversion	CO ₂ conversion	AE/photon
	(µW cm ⁻²)	center (nm)	photon (min ⁻¹)	(µmol g (Ni) ⁻¹ min ⁻¹)	increment	(×10 ⁻²⁰)
-	-	-	-	430.2	0.000	-
Bandpass filter	5810	332	3.24×10 ¹⁷	435.8	0.013	4.1
331.6 nm						
U340	45961	350	2.44×10 ¹⁸	473.3	0.101	3.7
L42+B440+HA30	60029	450	4.12×10 ¹⁸	515.9	0.199	4.8
G545	29768	550	2.49×10 ¹⁸	441.3	0.026	1.0
R64+HA30	49738	660	4.99×10 ¹⁸	438.7	0.018	0.4

enhancement induced by one photon (AE/photon)

Catalyzata	Particle size (nm) ^a					
	Before reaction	Thermal	Photo +thermal			
Ni@SiO ₂ -	49.8	52.1	51.2			
Core		32.1	51.5			
Ni@SiO ₂ -	37.6	38 /	28 1			
Yolk		50.4	36.1			
Ni/SiO ₂ -Im	24.3	32.8	35.5			

Table S2 Particle sizes of the Ni/SiO₂ catalysts before and after reaction.

a, calculated via Scherrer equation through the Ni diffraction peak at 44.7 °.

The Ni particle sizes over Ni@SiO2-Core and Ni@SiO2-Yolk before and after reaction were similar, and

it revealed that Ni particles were not aggregated. Ni aggregation is not responsible for catalyst deactivation.



Fig. S1 XRD patterns of Ni nanoparticles.

After calcination at 500 °C for 1 h, hexagonal Ni transformed into cubic Ni.



Fig. S2 (a), (c) and (e) TEM images of Ni/SiO₂-Im, Ni@SiO₂-Core and Ni@SiO₂-Yolk catalysts, and the

relevant Ni particle size distributions (b), (d) and (f).



Fig. S3 Ni 2p XPS spectra of Ni/SiO₂ catalysts.



Fig. S4 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of support SiO₂ and Ni/SiO₂

catalysts.



Fig. S5 Catalytic activities of Ni@SiO₂-Core, Ni@SiO₂-Yolk and Ni/SiO₂-Im in CRM with the irradiation of light of various intensities.

Reaction conditions: 550 °C, CH₄/CO₂=1, flowrate 20.0 mL/min, catalyst containing 0.030 g metallic Ni, with or without light irradiation (light wavelength 300 nm $< \lambda < 800$ nm).



Fig. S6 Detected temperature over Ni/SiO₂-Im with the irradiation of light of different intensities (without extra heat supply).

With the irradiation of light of the same intensity, the temperature increases over other Ni@SiO₂ catalysts were comparable with that Ni/SiO₂-Im (\pm 1°C).

Supposing it is photo-induced temperature increase or local heating that enhanced the catalytic performance of Ni/SiO₂ with light irradiation, then the activity increase slopes over the Ni/SiO₂ catalysts were expected to be similar (since the temperature increments were nearly the same over the Ni/SiO₂ catalysts, in Fig. S6, and active site determines activity in a thermal-driven catalysis), however, in this research they did not follow such a rule (Fig. 2 and Fig. S5). That is, it was not photo-induced temperature increase or local heating that enhanced the catalytic performances of Ni/SiO₂ catalysts.



Fig. S7 Detected temperature with the light irradiation of 1.07 W cm⁻² (with extra heat supply to compensate the reaction temperature to 550 $^{\circ}$ C).

The results in Fig. S7 indicated that the incremented temperature was compensated by a temperature controller to the well calibrated reaction temperature 550 °C. That is, the sum of the heat from light and heater remained constant at 550 °C. The higher the temperature increment by light irradiation, the less heat that supplied from the heater.



Fig. S8 In-situ ESR profiles of bulk Ni under dark condition and with light irradiation in CH₄ atmosphere

(the two peaks at 315.0 and 319.3 mT were attributed to the reference Mn).



Fig. S9 (a) CO₂ conversion over Ni@SiO₂-Core and Ni@SiO₂-Yolk, magnified Fig. 2 (b) in the main text, (b) CO₂ conversion losses over Ni@SiO₂-Core and Ni@SiO₂-Yolk.

Reaction conditions: 550 °C, CH₄/CO₂=1, flowrate 20.0 mL/min, catalyst containing 0.030 g metallic Ni, with or without light irradiation (light wavelength 300 nm $< \lambda < 800$ nm, intensity 1.07 W cm⁻²).

 CO_2 conversion loss is defined as the difference between initial (1.0 h) and finial (5.0 h) CO_2 conversions. The lower CO_2 conversion loss, the better the stability of the catalyst. From Fig. S9(b), it could be seen that, CO_2 conversion loss decreased with light assistance, which indicated that the stability of the catalysts was improved.



Fig. S10 TEM image of (a) spent Ni@SiO₂-Core after 0.5 h CRM and (b) spent Ni/SiO₂-Im after 5.0 h CRM.



Fig. S11 Schematic illustration for the formation of deposited carbon on spent Ni/SiO₂ catalysts, (a) encapsulation-structured Ni@SiO₂-Core and Ni@SiO₂-Yolk catalysts, and (b) Ni/SiO₂-Im catalyst.



Fig. S12 Mechanism for the growth of carbon nanotube over Ni@SiO2-Core and Ni@SiO2-Yolk catalysts in

thermal-driven condition.

References

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