Supporting Information for:

Sustainable Synthesis of a Highly Stable and Coke-Free Ni@CeO_2 Catalyst for Efficient Carbon Dioxide Reforming of Methane

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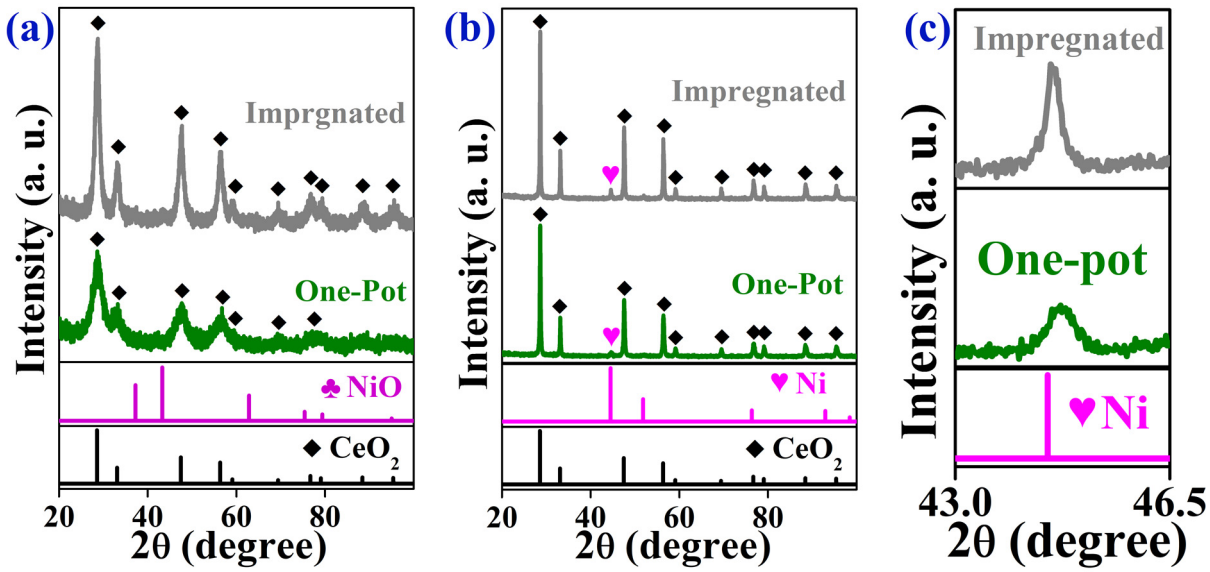

Figure S1. PXRD patterns of calcined (a) and reduced (b), Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts. (c) PXRD patterns of the reduced Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts at a slow scanning speed of 0.6 °/min (2θ= 43.0 – 46.5°).

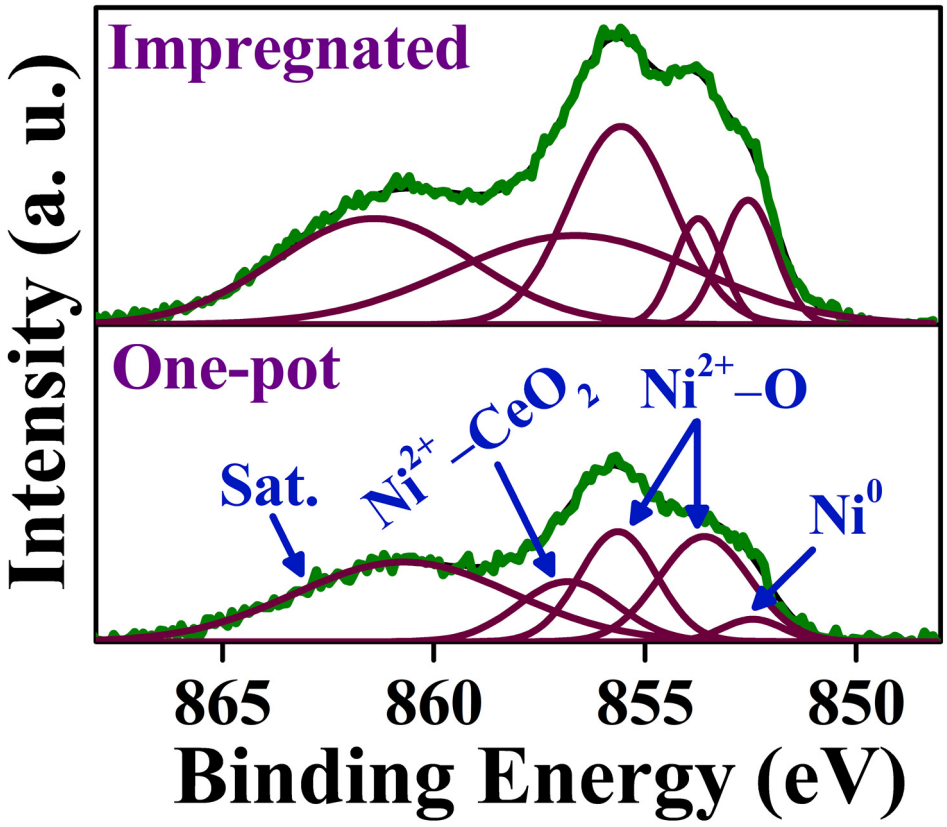

Figure S2. XPS spectra of Ni 2p in the reduced Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts.

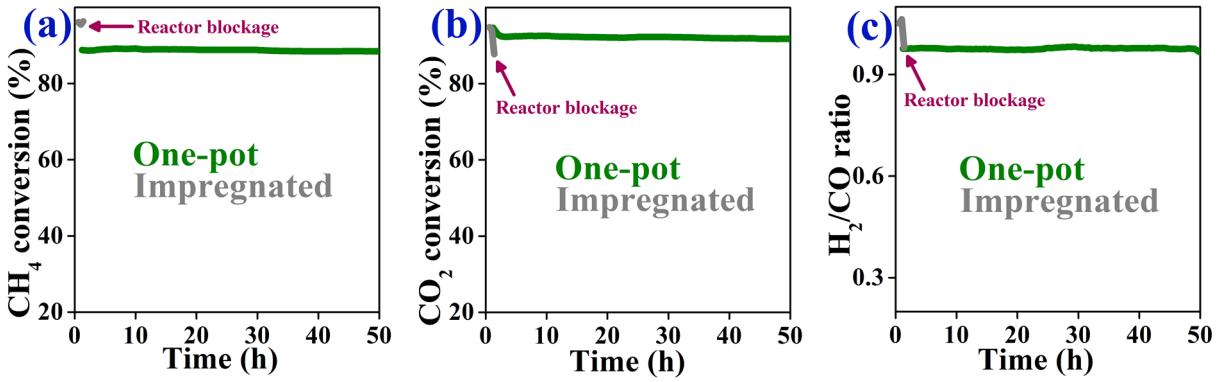

Figure S3. CH_4 conversions (a), CO_2 conversions (b), and H_2/CO ratios of Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts at a reaction temperature of 800 °C and WHSV of 24,000 mL g_{cat}^{-1} h^{-1} for 50.0 h.

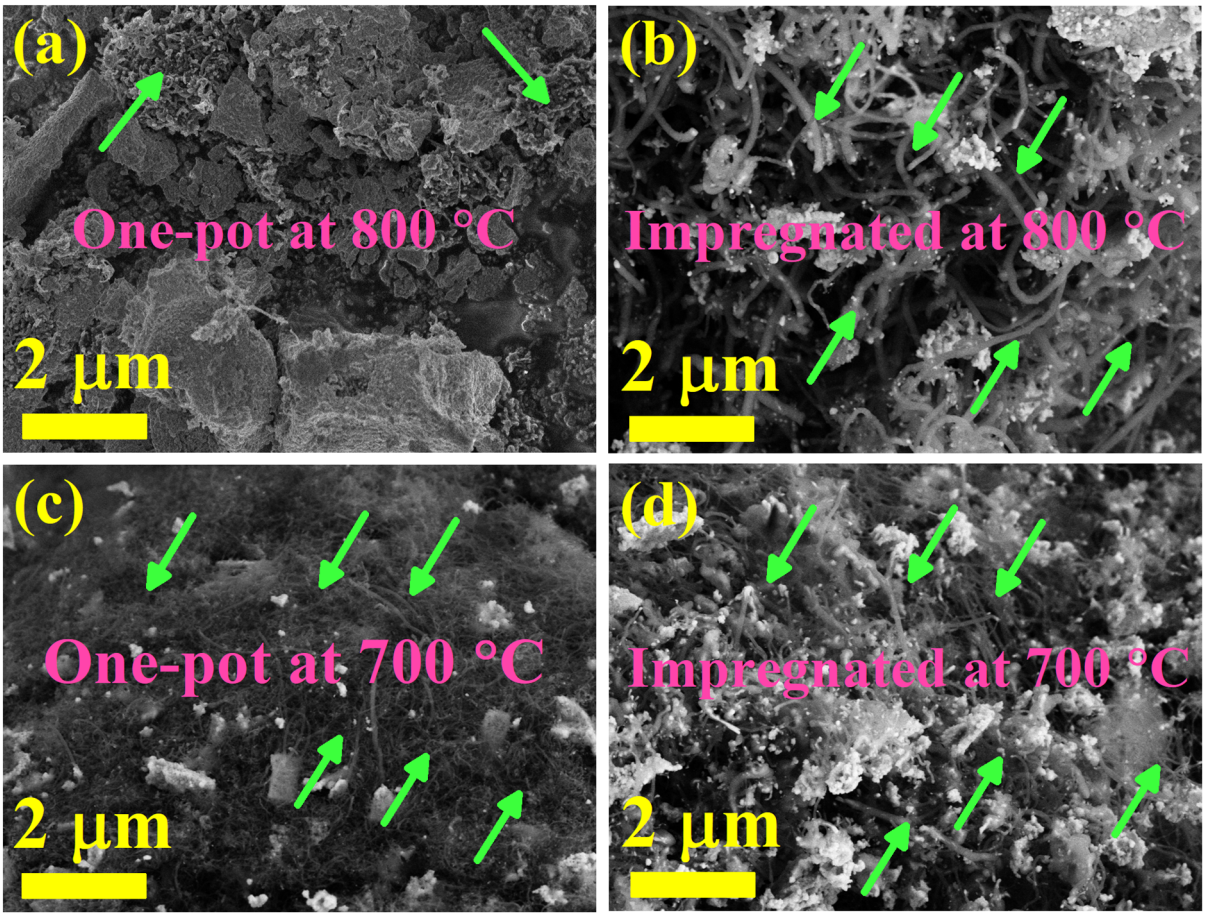

Figure S4. FESEM images of Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts after operating the DRM reaction for 50.0 h, at temperature of 800 °C (a and b) and 700 °C (c and d). The green arrows refer to the carbon filaments deposed on the catalysts' surface after the reaction.

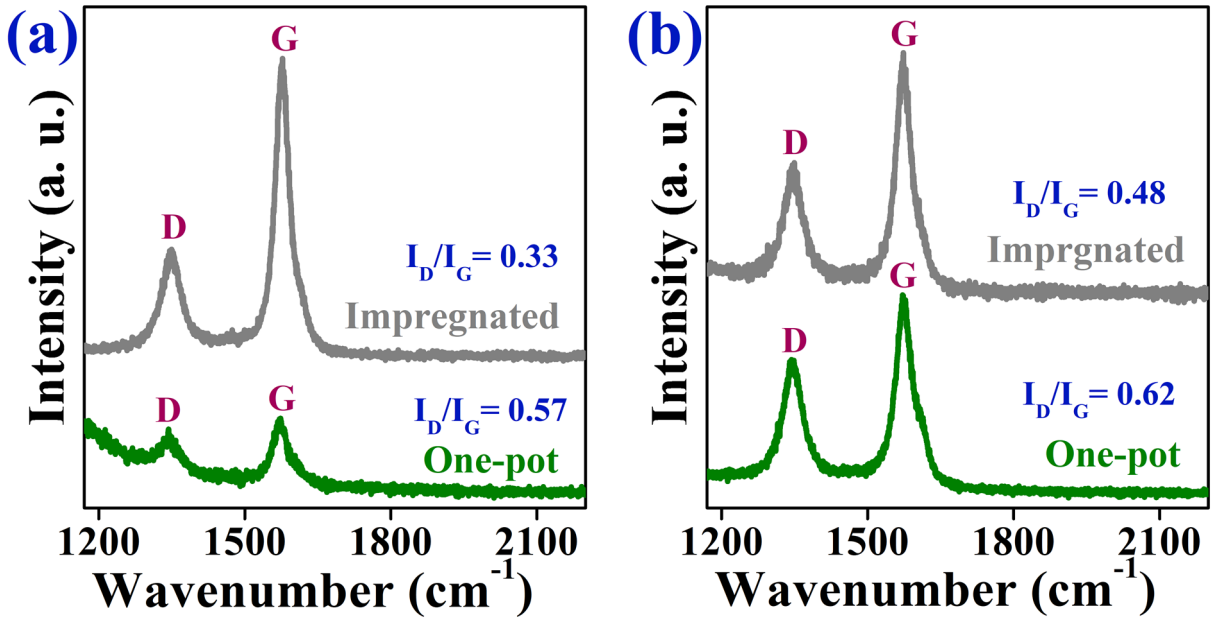

Figure S5. Raman spectra of Ni@CeO_2/12.5 (One-pot) and Ni/CeO_2/12.5/Impreg (Impregnated) catalysts after operating the DRM reaction for 50.0 h, at temperature of 800 °C (a) and 700 °C (b).

Table S1. BET surface area, total pore volume, and average pore diameter of the calcined and reduced samples.

Material	Calcined samples			Reduced samples		
	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
CeO_2	57.9	0.072	5.0	2.74	0.026	38.6
Ni@CeO_2/2.5	78.8	0.093	4.7	3.02	0.029	38.9
Ni@CeO_2/7.5	79.7	0.085	4.3	2.47	0.025	40.4
Ni@CeO_2/12.5	66.9	0.073	4.4	2.10	0.020	38.6
Ni@CeO_2/20	58.5	0.057	3.9	1.50	0.017	44.1

Table S2. Crystal sizes of CeO_2 after calcination and reduction evaluated by Scherrer's equation based on XRD patterns.

Material	Calcined samples	Reduced samples
Ni@CeO_2/2.5	5.8	48.1
Ni@CeO_2/7.5	4.8	42.8
Ni@CeO_2/12.5	4.3	39.8
Ni@CeO_2/20	3.9	38.1
Ni@CeO_2/12.5/Impreg.	10.4	47.9

Table S3. Comparison of the DRM catalytic activity of our catalyst with recent Ni/CeO_2-based catalysts reported in literature.

Catalyst	Reaction temperature (^oC)	CH_4 conversion (%)	CO_2 conversion (%)	H_2/CO ratio	Carbon deposition (mg/g_{cat} h)	Reference
$Ni@CeO_2$/7.5	**800**	**86.5**	**91.8**	**0.98**	**0**	**This work**
$Ni@CeO_2$/7.5	**700**	**58.3**	**64.2**	**0.91**	**0**	**This work**
Ni/CeO_2 Nanoflakes	800	42	76	0.67	2.75	1
$Ni@CeZrO_2$	800	53	66	0.74	1.6	2
$Nd/Ni/CeZrO_2$	650	24	52	00.74	21.3	3
Ru/CeO_2	700	39	48	-	-	4
$NiIn/CeO_2$-Al_2O_3	650	19	33	0.50	2.5	5
Ni-CeX-Y/SiO_2	750	78	80	0.95	0.25	6
Pt/CePr/Al_2O_3	800	57	68	0.79	0.09	7
PSC CeO_2–NiO	750	92	85	0.89	0.37	8
Ni/CeO_2-Al_2O_3	800	69	82	0.69	0	9
Ni/CeO_2/YSZ	750	62	73	-	1.5	10
Ni/CeO_2	800	72	80	0.91	0	11
Pt-Ni/CeO_2	650	54	57	0.75	0	12
Ni-CeO_2	500	30	42	0.71	15.4	13

Table S4. Comparison of the DRM catalytic activity of our catalyst with recent Ni/CeO_2-based catalysts reported in literature.

	T (℃)	WHSV[a] (L g_{cat}^{-1} h^{-1})	CH_4 /CO_2 (v/v %)	TGA weight loss (%)	TOS[b] (h)	[c] (mg_{coke})	[d] (mg_{coke} g_{cat}^{-1} h^{-1})	[e] (mg_{coke} g_{cat}^{-1} $g_{carbon\ fed}^{-1}$ h^{-1})	Ref
Ni@CeO2/2.5	700	24	33.3/ 33.3	0	50	0	0	0	This work
Ni@CeO2/7.5				0	50	0	0	0	
Ni@CeO2/12.5				28.13	50	29.36	7.83	0.2435	
Ni@CeO2/20				26.94	2	27.66	184.37	143.37	
Ni@CeO2/2.5	800			0	50	0	0	0	
Ni@CeO2/7.5				0	50	0	0	0	
Ni@CeO2/12.5				3.50	50	2.72	0.73	0.0226	
Ni@CeO2/20				28.10	11	29.31	35.53	5.0233	
Ti-CAT-II	700	39	46.2/ 46.2	25	7	33.33	47.62	0.5038	14
Ti-CAT-III				15	7	17.65	25.21	0.2667	
Flakes	800	60	12.5/ 12.5	5.5	20	5.82	2.91	0.0091	1
$Ni/Ce_{0.8}Ti_{0.2}O_{2-\delta}$, d = 22 nm	750	30	40/ 40	-	100	2	0.2	0.0016	15
Ni/CeO_2	800	150	40/ 40	19.4	50	12.03	4.81	0.0006	16
Ni/La-DC				2.0	50	1.02	0.41	0.0001	

[a] Weight hourly space velocity, including diluents (N_2, He, etc.)

[b] Time on stream

[c] Coke deposited in an entire reaction

[d] Coke formation rate

[e] Coke formation rate, divided by carbon fed