Electronic Supplementary Information

Coking-resistant dry reforming of methane over BN-nanoceria interface-confined Ni catalysts

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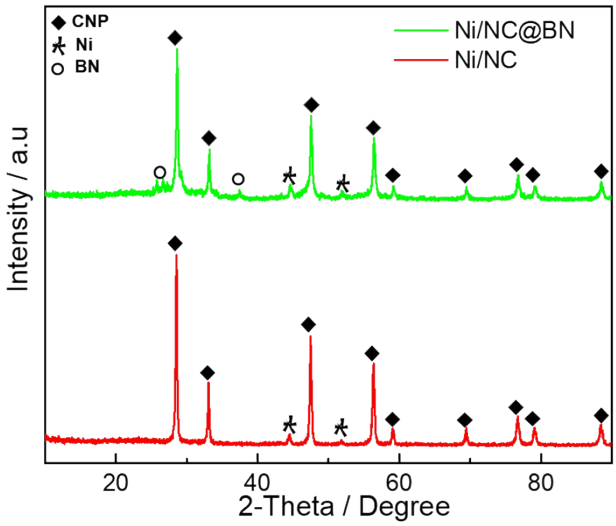

Fig. S1 XRD patterns of Ni/NC and Ni/NC@BN catalysts.

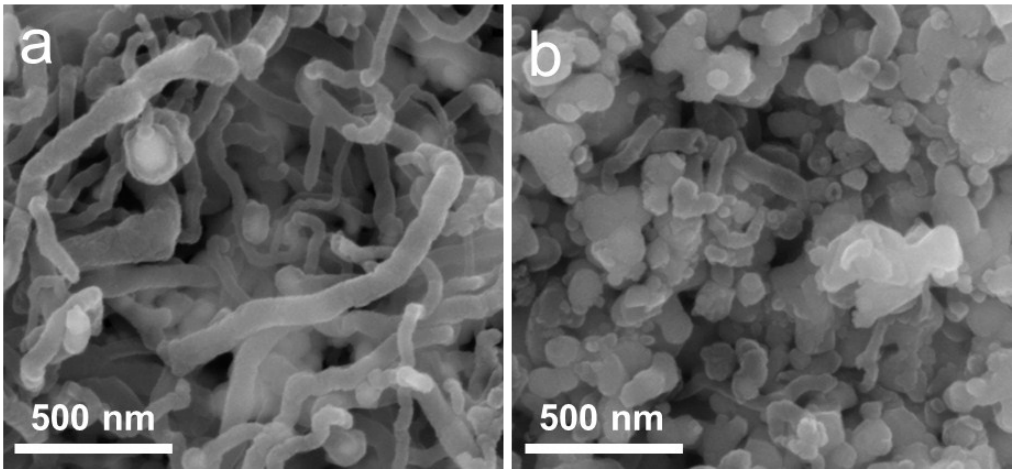

Fig. S2 SEM images of (a) the spent Ni/NC catalyst after 20 h DRM reaction and (b) the spent Ni/NC@BN catalyst after 100 h DRM reaction.

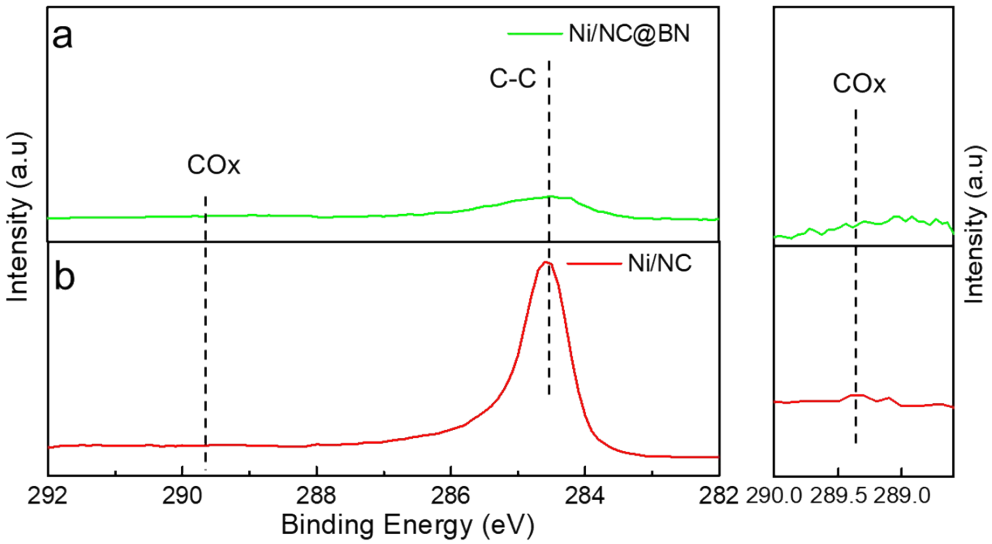

Fig. S3 C1s XPS spectra of (a) the spent Ni/NC@BN catalyst after 100 h of DRM reaction and (b) the spent Ni/NC catalyst after 20 h of DRM reaction and zoomed in spectra in the range of 288–291 eV.

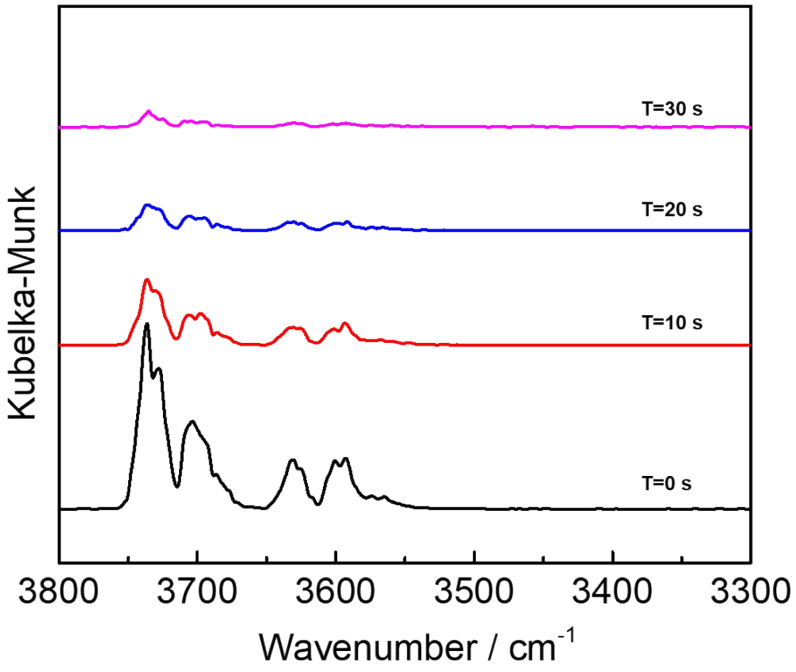

Fig. S4 Enlarged figures of transient reactions over Ni/NC@BN and Ni/NC catalysts.

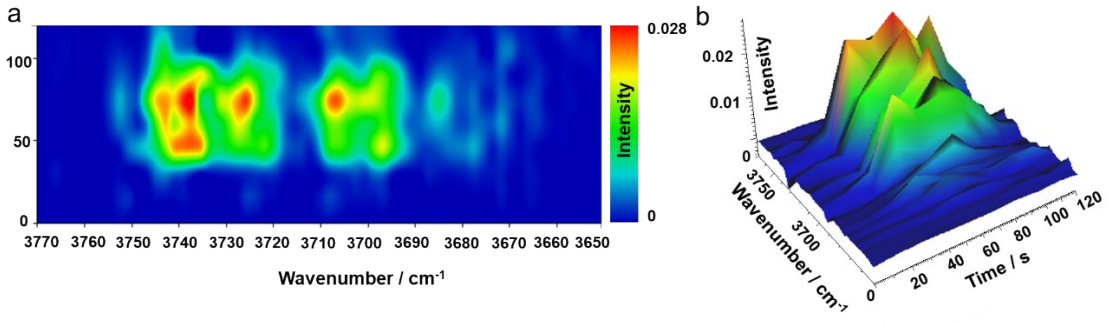

Fig. S5 (a) 2D and (b) 3D *in situ* DRIFTs of DRM reaction over Ni/NC@BN catalyst where CH_4 and CO_2 with a flow rate of 25 mL/min was adsorption on the catalyst at 650 ^oC for 1 min and then CO_2 feed was switched off.

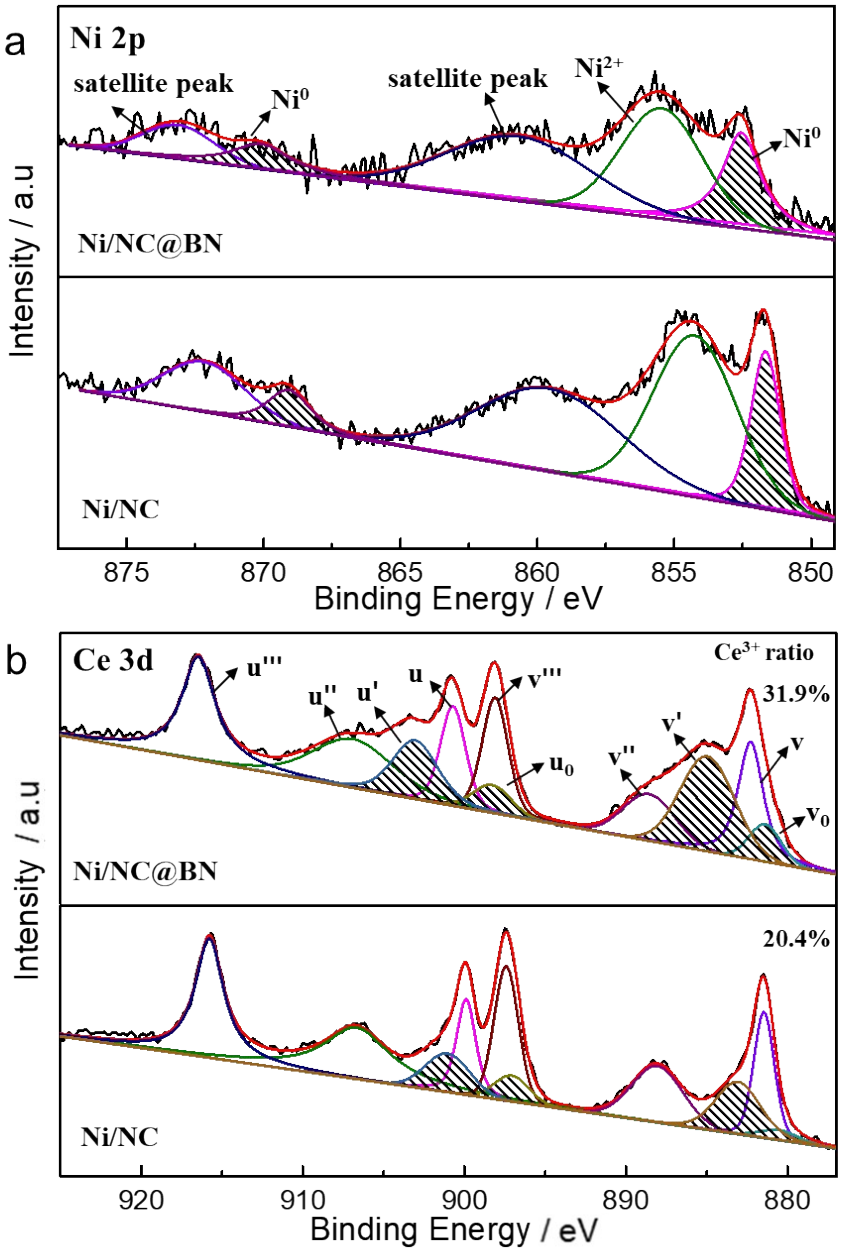

Fig. S6 XPS spectra for (a) Ni 2p and (b) Ce 3d of Ni/NC and Ni/NC@BN catalysts.

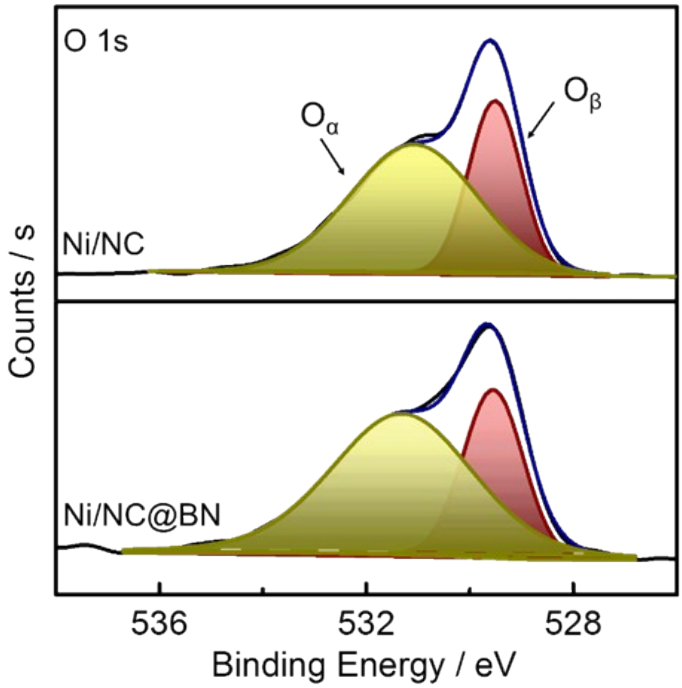

Fig. S7 O 1s XPS spectra of Ni/NC and Ni/NC@BN catalysts.

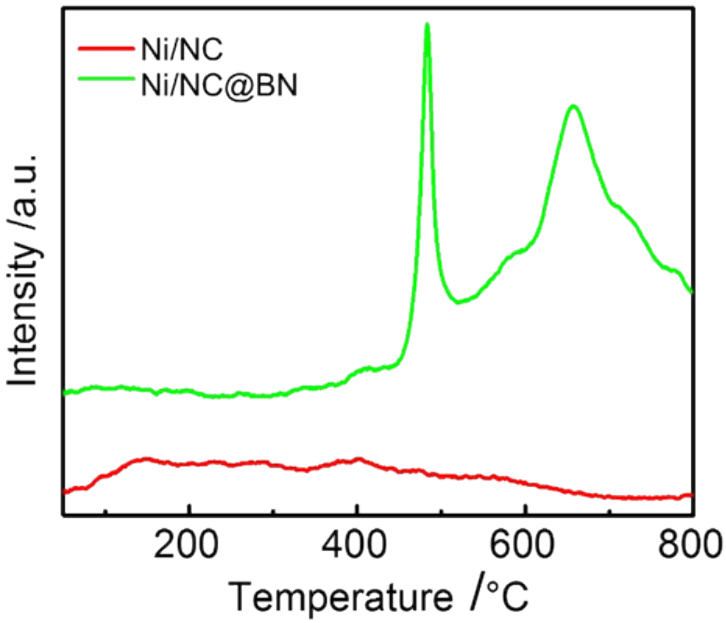

Fig. S8 O_2-TPD profiles of Ni/NC and Ni/NC@BN catalyst.

Table S1 The concentration of O_α from XPS and the corresponding desorption quantity of O_2 from O_2-TPD.

Catalyst	Concentration of O_α (%)	O_2 desorption quantity (mmol/g)
Ni/NC	64.6%	0.074
Ni/NC@BN	68.7%	0.106

Table S2 The TOF_{CH4} of the as-prepared catalysts during the DRM reaction at 550 °C and textural properties of the reduced catalysts.

Catalysts	Ni loading [a] (%)	Temp. (°C)	Time X (h)	Specific surface area [b] (m^2 g^{-1})	Ni dispersion [c] (%)	CH_4 conversion [d] (%)		TOF $_{CH4}$ [e] (h^{-1})
						Initial	after 6h reaction	
Ni/NC	6.83	550	6	16.8	1.45%	19.4	7.1	3217
Ni/NC@BN	7.31	550	6	16.4	0.42%	13.8	9.8	14218

[a] Ni loading were measured by ICP.

[b] Specific surface area of the catalysts determined by the BET method.

[c] Ni dispersion was measured by H_2 pulse chemisorption.

[d] The CH_4 conversion was tested at 550°C with a CH_4 flow rate of 45 mL/min.

[e] The value of TOF was tested at 550°C with a CH_4 flow rate of 45 mL/min.

The textural properties of the as-prepared catalysts were investigated by N_2 adsorption–desorption techniques. As shown in Table S1, the BET specific surface area of Ni/NC was 16.8 m^2 g^{-1} and the BET specific surface area of Ni/NC@BN was 16.4 m^2 g^{-1}. The Ni dispersions of Ni/NC and Ni/ NC@BN catalysts are 1.45% and 0.42%. The dispersion value of Ni/NC@BN was a bit lower than that of Ni/NC. The reduced ability of hydrogen chemisorption for Ni/NC@BN catalyst is likely caused by the strong metal support interaction (SMSI) between nickel and CeO_2, which blocks the Ni active sites for hydrogen chemisorption[1, 2]. In addition, the better coke resistance of Ni/NC@BN could be attributed to the –OH species on the surface of BN. The strong interaction between Ni and BN-nanoceria (NC) interfaces plays a key role in suppressing metal sintering. Therefore, the excellent coking and sintering resistance makes the catalyst maintain better stability.

References

[1] S. Das, J. Ashok, Z. Bian, N. Dewangan, M.H. Wai, Y. Du, A. Borgna, K. Hidajat, S. Kawi, Silica–Ceria sandwiched Ni core–shell catalyst for low temperature dry reforming of biogas: Coke resistance and mechanistic insights, Appl. Catal. B-Environ. 230 (2018) 220-236.

[2] H. Ay, D. Üner, Dry reforming of methane over CeO_2 supported Ni, Co and Ni–Co catalysts, Appl. Catal. B-Environ. 179 (2015) 128-138.