

**MOFs-derived hierarchical hollow spheres composed of carbon-
confined Ni nanoparticles for efficient CO₂ methanation**

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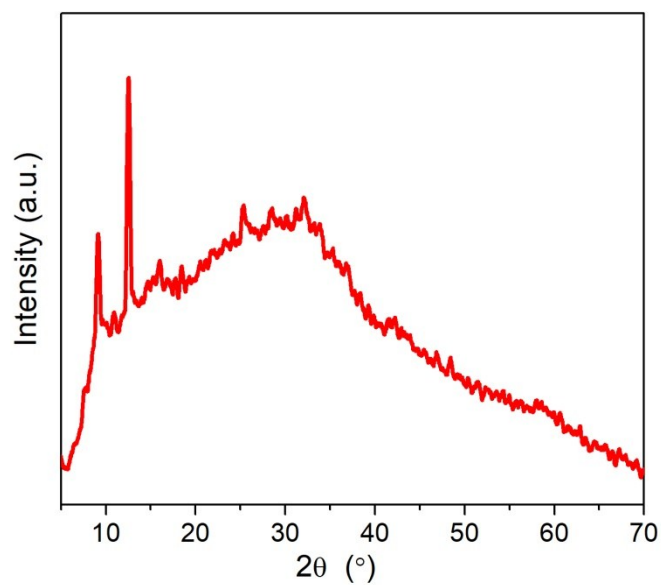


Fig. S1 XRD pattern of Ni-MOF.

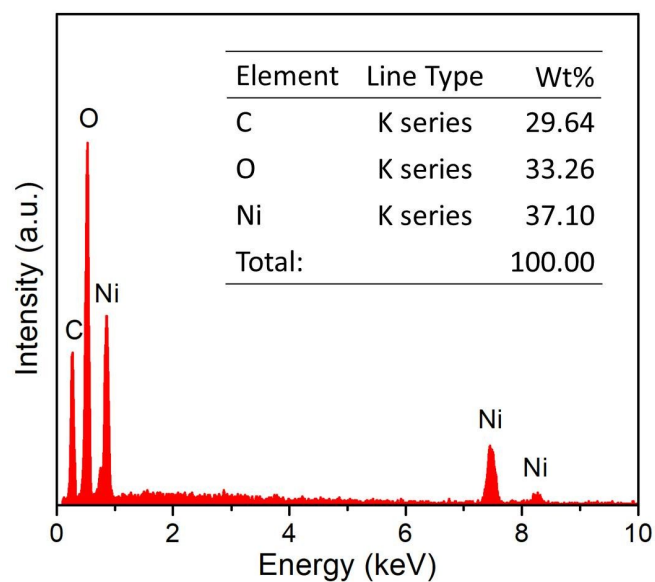


Fig. S2 EDX spectrum of Ni-MOF. Inset shows the corresponding weight contents of the elements.

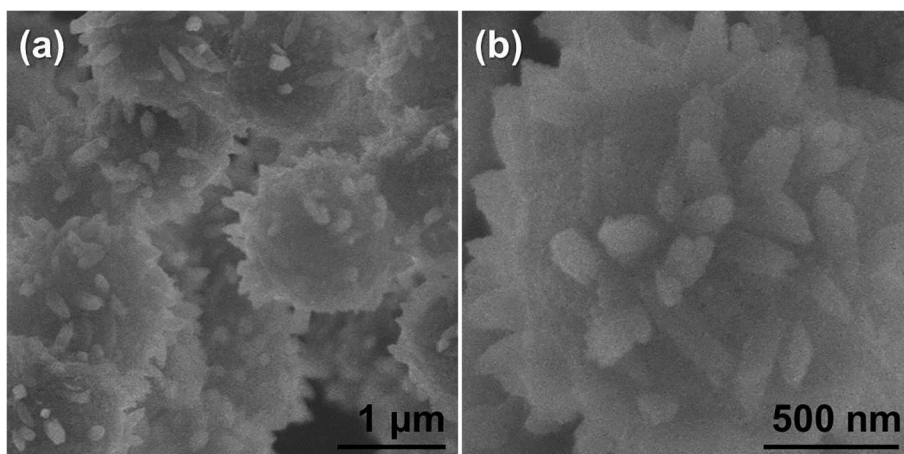


Fig. S3 FESEM images of hierarchical Ni-MOF microspheres.

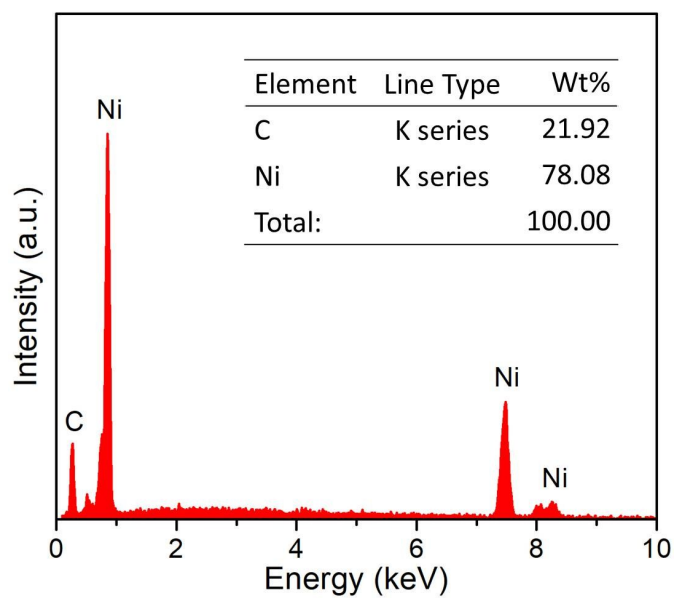


Fig. S4 EDX spectrum of Ni@C. Inset shows the corresponding weight contents of the elements.

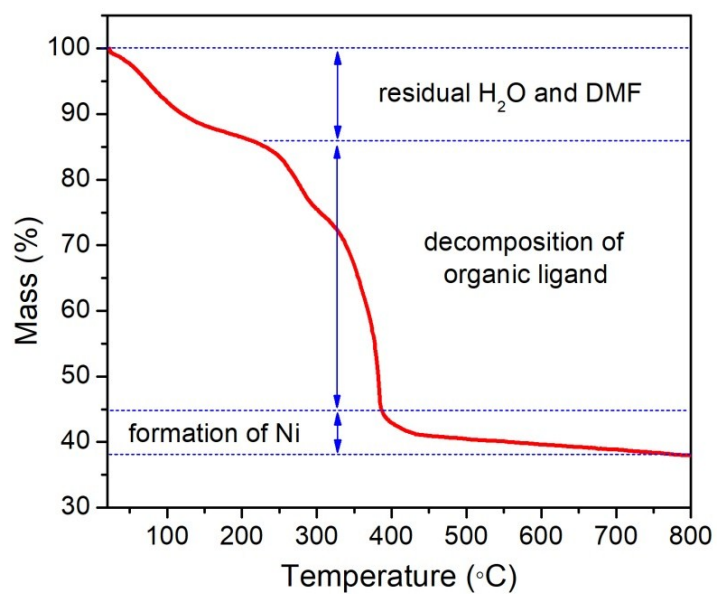


Fig. S5 TGA results of Ni-MOF in a N₂ atmosphere with a heating rate of 5 °C min⁻¹.

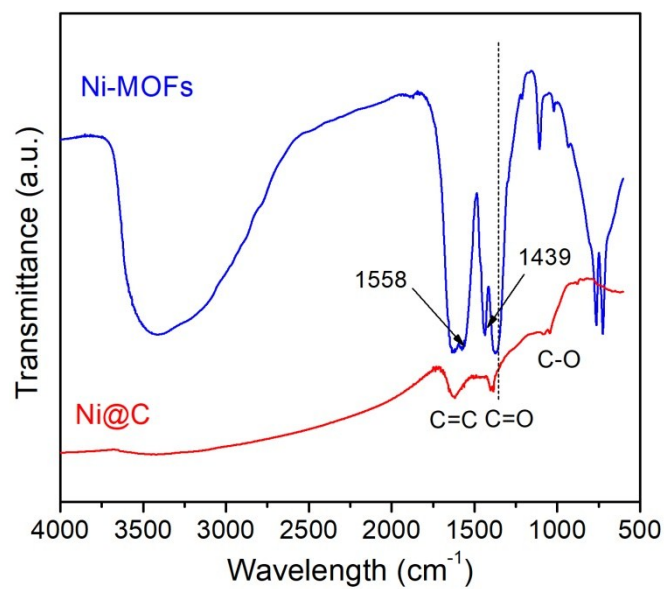


Fig. S6 FT-IR spectra of Ni-MOF and Ni@NC samples.

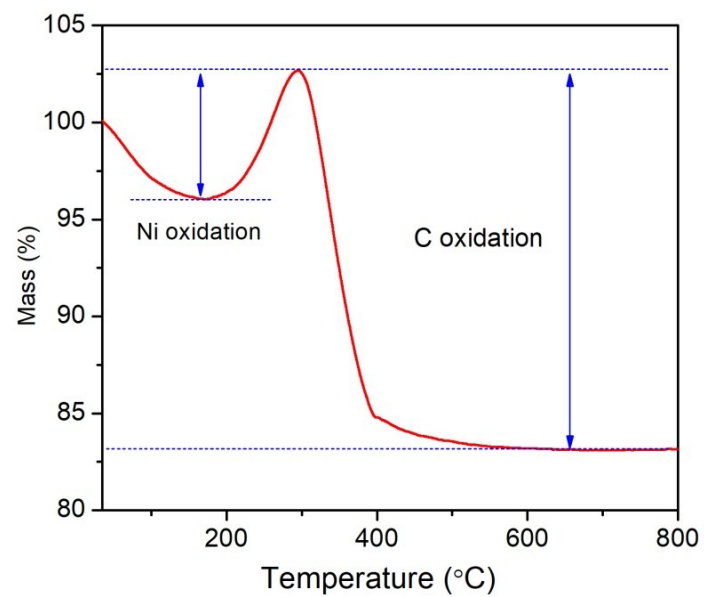


Fig. S7 TGA results of Ni@C in an air atmosphere with a heating rate of 5 °C min⁻¹.

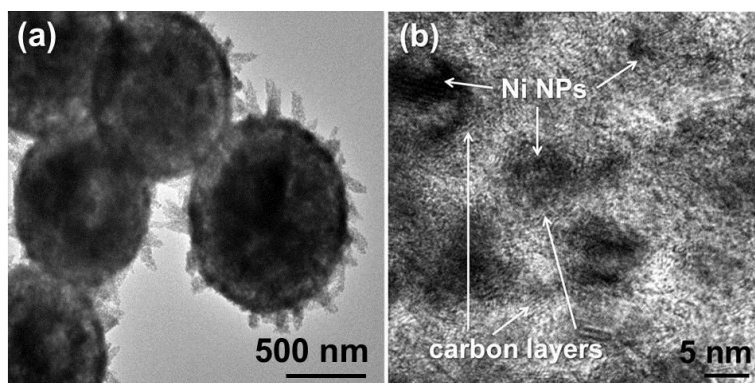


Fig. S8 (a,b) TEM images of hierarchical Ni@C microspheres.

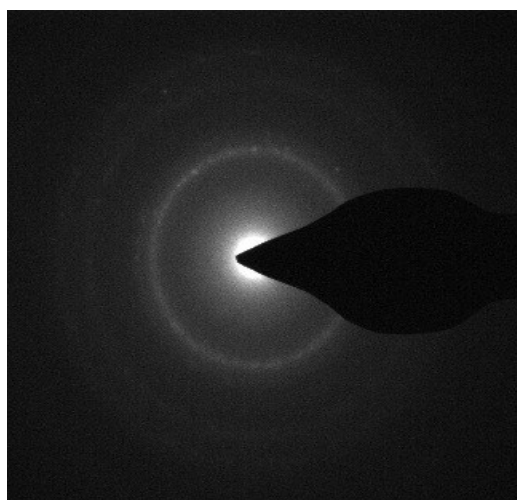


Fig. S9 SAED pattern of Ni@C sample.

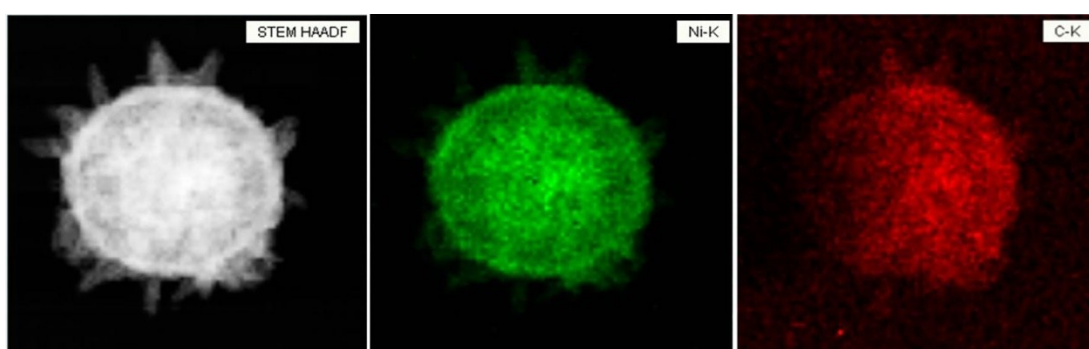


Fig. S10 Elemental mappings of an individual hierarchical Ni@C microsphere.

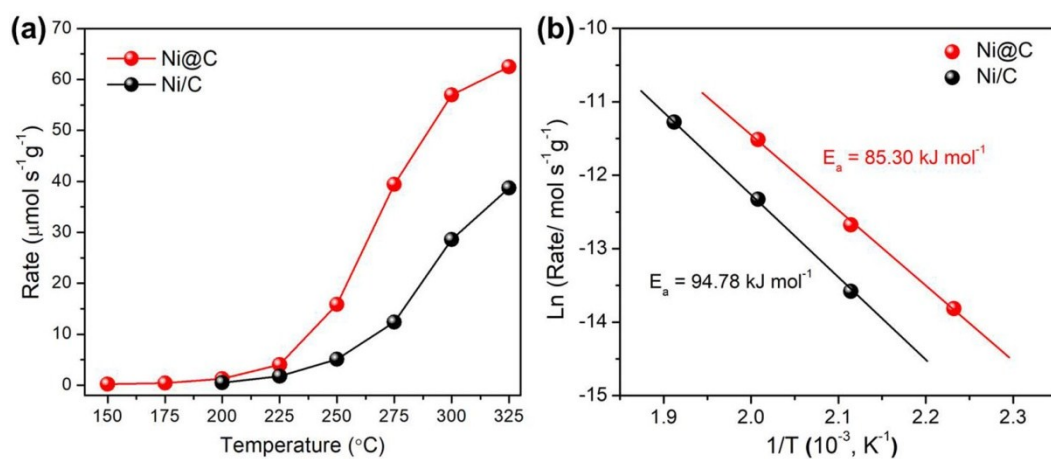


Fig. S11 (a) CO₂ methanation performance of Ni@C and Ni/C catalysts under different temperatures. (b) Arrhenius plots for CO₂ methanation over Ni@C and Ni/C catalysts.

Table S1. Comparison of CO₂ methanation performance of Ni@C with that of other Ni-based catalysts at atmospheric pressure.

Catalyst	Temp. (°C)	GHSV (mL g ⁻¹ h ⁻¹)	Con.CO ₂ (%)	Sel.CH ₄ (%)	TOF (10 ⁻³ s ⁻¹)	Ref.
Ni@C	300	33000	91.16	99.9	4.28	This work
12Ni4.5Ce/CNT ^a	350	30000	83.8	100	/	1
Ni/MSN ^b	300	50000	64.1	99.9	1.61	2
OMA-2Co8Ni ^c	400	15000	79.9	98.3	/	3
15%Ni/ZSM-5	250	2400	27.1	99	7.56	4
15%Ni/TiO ₂	260	2400	96	99	1.22	5
Ni _{0.8} Mg _{0.2} @SiO ₂	300	60000	87	99	/	6
Ni(21.7)@S16C ^d	500	36000	33	30	12	7
Ni/CeO ₂	350	10000	100	100	/	8
Ni-Al ₂ O ₃ -HT ^e	350	75000	82.5	99.5	5.7	9
7.5Ni2.5Fe/Al ₂ O ₃	250	32000	22.1	99	5.9	10

^a CNT: multi-walled carbon nanotubes.

^b MSN: mesostructured silica nanoparticles.

^c OMA: ordered mesoporous Al₂O₃.

^d S16C: the cage-type mesopores of –COOH-functionalized mesoporous silica SBA-16.

^e HT: hydrotalcite.

Table S2. The weight contents of the elements of four Ni@C samples (denoted as Ni@C-1[#], Ni@C-2[#], Ni@C-3[#] and Ni@C-4[#]) prepared in different batches.

Element	Line Type	Wt%			
		Ni@C-1 [#]	Ni@C-2 [#]	Ni@C-3 [#]	Ni@C-4 [#]
C	K series	20.40	20.92	23.10	22.97
Ni	K series	79.60	79.08	76.90	77.03
Total:		100.00	100.00	100.00	100.00

Supplementary references

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